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STARTUP SOLVENT SELECTION FOR THE LIQUEFACTION OF LIGNITE. Richard R. Dillon and Warren P. Scarrah. University of North Dakota, Grand Forks, N.D. 58201

COAL DESULFURIZATION IN THE P&M SOLVENT REFINING PROCESS

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I. INTRODUCTION

In the P&M Solvent Refined Coal Process, coal is dissolved under moderate hydrogen pressure in an internally generated heavy aromatic solvent to produce a liquid from which mineral matter is removed by filtration. Solvent is recovered from the filtrate by vacuum distillation; the distillation residue which can be handled in either solid or liquid form is a very low ash, low sulfur material known as Solvent Refined Coal (SRC). An objective of the laboratory program in support of the Solvent Refined Coal Pilot Plant program is the development of procedures for improved desulfurization of high sulfur coals. Many of the high volatile bituminous coals in the eastern half of the United States contain an appreciable amount of pyrites which can be removed from the coal by filtration after the coal is dissolved in a suitable solvent. Normally this process is conducted in the presence of molecular hydrogen and a naturally catalyzed hydrogenation reaction is an important factor in the proper solution of the coal. This reaction also increases the removal of sulfur which is a component of the organic phase of the coal. The arguments and supporting evidence for the existence of natural catalytic effects in such coals have been reported previously. 1,2,3,4,5,6/

Current laboratory studies are directed to the development of suitable operating procedures to use the naturally catalyzed reactions more effectively. The general requirements for such reactions have been outlined by laboratory studies and are being tested in some pilot plant operations. 7,8/ It is now possible to dissolve a number of high volatile bituminous coals and to recover the organic material from the coal using these arts. The preferred reactor designs and the best operating conditions are not presently well defined.

A sound basis for commercial scale processing of these coals depends on better understanding of the chemistry of the coal solution reactions as well as on the solution of a number of practical engineering problems. To a considerable extent the engineering problems appear to be basic elements of coal processes utilizing either natural catalysts or synthetic catalysts. Therefore progress in solving these problems in the Solvent Refined Coal Process should contribute to advancing related processes as well. Evaluation of natural catalysts suggests that some coals will be suitable for processing without resort to synthetic catalysts but that others will need to be catalyzed additionally. The operating rules are not presently sharply defined; therefore the separation between suitable and unsuitable coals can not be made without resorting to a program of practical tests in the laboratory.

Accordingly the laboratory program is designed to improve the art by studies of reactor combinations and process variables and to demonstrate the suitability of various coals for processing. Emphasis is placed on the use of natural catalysis in the hope that such processing will prove to be the cheapest route to purified coal derived fuels in a significant number of cases. The effect of specifications, such as sulfur limits, which may be imposed may determine the applicability of alternative processes in the future. It is necessary to know the technical limits for the process using natural catalysts and for alternative processes for this reason also. It is expected that various alternatives - catalysts, feedstocks, product quality requirements, and so on will be possible. An optimum plant design will require knowledgeable compromises between these alternatives. Sound data on the natural catalytic effects should comprise an essential component of the thinking which results in choosing a coal processing configuration.

The experimental section of this paper describes several recent experiments which were done to develop optimization procedures for the naturally catalyzed coal solution process. Such experiments must satisfy the constraint that a break-even amount of solvent be obtained and that the reactions be continued with solvent recycle until a steady state develops between the solvent, the coal, and the reaction conditions used. It is essential that the equilibrated solvent retain the capacity to donate hydrogen readily in the initial stages of the coal solution reaction. An additional constraint is that the product solution must remain filterable as the system is equilibrated. Several analytical procedures are used during reactor operation to follow the equilibration process. These produce data which allow the selection of representative samples for complete analysis and which can give advance warning in the event that unsuitable conditions or failing equipment are endangering the experiment. It is now occasionally possible to recognize problems in time to correct equipment or to select better operating conditions. Failure after a period of recycle operation may be observed if poor solvent reactivity results from the conditions in use, for example.

Although specific equipment and some detailed experimental data are to be presented, it is felt that the description of the operating methods may be of more general interest. Some of these procedures may be useful in related coal processing studies. The program of experiments involves changes in reactor combinations as well as the interplay of a number of variables. Rapid indications of trends facilitates decisions regarding the time to be spent in equilibration of the system before samples can be collected for analysis and give early indications of the utility of the conditions chosen for study in an experimental trial. Some rapid analytical methods have been developed which can be used to evaluate samples as the reactor is operated and which facilitate such studies. The results which are presented do represent some progress in improving sulfur removal from Kentucky coal. It is not expected that the conditions reported are optimized. Continued improvement should result from systematic explorations using these techniques. Applications to other coals are also planned as an extension of this program.

II. EXPERIMENTAL

A. Equipment

A simplified schematic diagram of the laboratory scale continuous reactor used in these experiments is shown as Figure 1. Excluded from the diagram are the slurry feed system and the hydrogen compression and metering system. A more complete description of the apparatus is presented in OCR Report No. 53 Interim Report No. 8. 4/ Coal dissolution and hydrogenation is accomplished in a two or three vessel reactor consisting of a preheater and one or two dissolvers operated in series. The preheater consists of an 18 foot coil of 13/64 ID high pressure tubing heated by a fluidized sand bath. The internal volume of this coil is about 110 ml. The first dissolver is an electrically heated autoclave of about 450 ml volume. This is a vessel 1½ inches ID X 15 inches tall. In control experiments reported in this paper the reactor system consisted only of these two vessels. Reacted material passes from the first dissolver to a two liter autoclave, which may be used as a surge vessel only, or which may also serve as a second dissolver. In the control experiments, product was removed from the autoclave by means of a dip tube which reached the bottom of the vessel. The autoclave was kept cool enough to prevent additional reaction in this mode of operation. When the autoclave was used as a second dissolver it was heated sufficiently hot to allow reactions to proceed. Product was allowed to fill the vessel to a level established by an alternate dip tube ten centimeters from the bottom of the autoclave. This allowed the accumulation of about 565 ml of liquid in the autoclave. In the control experiments all liquid product was collected in the sample flask at near room temperature, and light oils in the product distribution were found by distillation of the sample. In the latter experiments under consideration a flash vessel was added to the reactor system to allow continuous separation of these fractions as the samples were made. This modification caused little variation in results except for a tendency for loss of some of the most volatile product which had previously been collected in a dry ice cold trap in the distillation of samples in the laboratory. In either mode of operation the gas is separated from the liquid stream as it is collected in the sample flask or in the flash vessel and is passed through a condenser before it is collected in a rubberized fabric bag. Samples are collected for timed intervals and when samples are not being collected the liquid is diverted to an alternate receiver while the gas which is disengaged flows to a vent line. Hydrogen is mixed at a Tee between the slurry feed pump and the preheater and has the chance to react in each of the heated vessels. Some additional hydrogen is metered into the system as a gage line purge and this contacts only the contents of the two liter autoclave. This is set to deliver one mole of hydrogen per hour, an amount which is small compared to the input before the preheater.

B. Materials Used

Kentucky coal from the Colonial Mine was used. An analysis is given in Table I. This coal is ranked as a high volatile B bituminous coal. Coal was ground to pass 150 mesh. The coal was sieved and air dried in the process to an average moisture content of 1.5% to 2.0%. Solvents were recycled in the process and after a number of passes the identity of the initial solvent is lost. In the control experiments the initial solvent was Gulf FS 120 Carbon Black Feedstock for the series which ended with CU 77, or a blend of FS 120 and crude anthracene oil for the series which ended with CU 90. The series of experiments, CU 91 through CU 93 was started with a partially hydrogenated anthracene oil. The properties of these starting solvents are summarized in Table II. One of the objectives of the experiments in this series was the demonstration that the initial solvent would be converted in the process and that the equilibrated solvent would have a composition determined by the operating conditions and the coal used. This was the reason for starting different experimental sequences with different initial solvents or with solvent mixtures.

C. Procedure and Product Workup

Although coal dissolution is accomplished in a continuous process, product workup is a batch process. Coal slurry and hydrogen are fed continuously to the reactor which is controlled at the desired pressure and temperatures. Product coal solution is accumulated in a product receiver over an interval of 3 or 4 hours. The coal product solution is taken to the laboratory for workup which may include the following operations: stripping to remove water and light oils formed in the process, filtration to remove the ash and the small amount of undissolved organic matter, and distillation to recover solvent from the coal solution. The residue from this vacuum distillation is the principal Solvent Refined Coal Product. Some excess of light oil above the amount needed for recycle as solvent may also be obtained.

In order to more rapidly attain a recycle solvent equilibrated with the coal and the reaction conditions, the filtration step may be eliminated, with solvent being recovered from stripped unfiltered coal solution. This is mixed with coal and returned to feed slurry until the system is judged to be equilibrated. An experiment is continued at one set of conditions with recycle of solvent until reaction control parameters indicate a stable reaction has been achieved. A product or products may be collected at this condition and subjected to the standard SRC workup including filtration for determination of product properties and distribution. A variable is then changed and solvent is again recycled until a new steady state appears to have been established. Typically an experiment will be continued for about 100 hours during which two condition sets may be equilibrated.

The stripping procedure provides two light oil cuts; "cold trap oil" which is not condensed by a water cooled condenser at the vacuum distillation pressure (nominally less than 3mm Hg) but is condensed in a dry ice trap, and "cut 1 oil" which is that distilling up to 90°C at less than 3mm Hg and condensed by the water cooled condenser. If needed, some of the cut 1 oil may be used to maintain a balance of recycle solvent.

Recycle solvent is that collected between the endpoint for cut 1 oil and an upper limit in the range of 250°C to 300°C at typical vacuum pump pressures. When distillations are carried out from unfiltered coal solutions some decomposition is noted and distillations are terminated when the evolution of gases becomes significant. This can be followed by use of a suitable vacuum gage or by noting the formation of light products which appear as a smoke like vapor in the condenser and solvent receiver. The decomposition point determines the maximum practical amount of solvent which can be reclaimed in this circumstance. In distillation of filtered solutions the solution appears more thermally stable, and the decomposition point is observed at a higher temperature than is the case with the mineral matter present. When several filtered samples are collected it is usual to stop the distillation at a standard temperature chosen to produce at least a break-even amount of solvent. Vacuum bottoms are evaluated by elemental analysis and by melting point determination. This information allows an estimation of the availability of more solvent from the vacuum bottoms if necessary. The melting point of vacuum bottoms is increased as solvent is removed, and break-even amounts of solvent usually are not obtained until the melting point is about 185°C to 200°C. The interplay between the degree of reaction with hydrogen, conversion to solvent, and depolymerization or repolymerization effects must be taken into account in obtaining a solvent balance, therefore it is difficult to use a standard temperature in all cases. The objective of the reclaim procedure is to obtain the necessary amount of solvent and remain within practical operating limits of vacuum flash equipment. If this can not be achieved the operating condition set must be abandoned as unsuitable for use.

In the equilibration procedure the reclaimed solvent is mixed with coal and returned to feed slurry. It is a simple matter to compare the weight of slurry fed in the preparation of a sample with the weight of slurry returned from the reformulated cut 2 oil. It is usually possible to establish a temperature at which a solvent balance can be maintained, or to determine that no practical finish temperature will allow a balance, as the initial samples in the equilibration series are being distilled. As the equilibration process is continued a drift in yield or composition may be observed, as well as oscillation in these observations. Such adjustments from sample to sample are usually small. In the situation that more than a break-even amount of solvent is obtained, the weight of slurry in the feed vessel will increase. This is therefore an unambiguous indication that the conditions in use satisfy the constraint that at least a break-even quantity of solvent be obtained.

D. Discussion of Analytical Tools Used

One of the problems in working with the continuous reactor system has been the development of methods by which the reproducibility of the product could be established and which could be used to indicate when the product was equilibrated with feeds and the effect of reaction conditions. This problem is of particular importance in the current type of study in which the objective is preparation of well equilibrated samples. Two measurements which can be made rapidly on unfiltered coal solutions have been found to be particularly valuable in following the reaction while it is in progress. These are both based on spectrophotometric measurements. The methods are based on measurements taken from infrared spectra and measurements made in the visible region. Infrared spectra are obtained on thin films of unfiltered coal solution supported between polished rock salt plates. Of particular interest are bands in the CH stretching region. The ratio of the nonaromatic CH stretching band at about 2920 cm^{-1} to the aromatic CH stretching band at about 3050 cm^{-1} is determined and is reported as the term $\overline{IR}$. This value increases as the hydrogenation of the coal solution increases and decreases as the hydrogenation decreases (and aromaticity increases). Plots of $\overline{IR}$ versus time indicate if the hydrogenation level of the product is increasing, decreasing, or has stabilized. Spectra can be obtained in a few minutes and use only a drop of sample. It is therefore easy to develop an observation rapidly and economically by this method and to make reliable estimates of the amount of hydrogen acquired or lost by the solution.

"Blackness" is a measure of absorbance of the coal solution in the visible region. It was found that colored material in the coal solution could be dissolved and measurements in the visible region could be used to follow the concentration of a fraction of dissolved coal in the reaction product stream. These solutions absorb throughout the visible region, therefore the absorbance is arbitrarily measured at 550 nanometers. Measurements are made in solution in pyridine in ½ inch square cuvettes using a B&L Spectronic 20 spectrophotometer.

$$\text{Blackness} = \frac{(\text{Optical Density})(\text{Volume of Pyridine Soln. in ml})}{(\text{Sample size in grams})\ 100}$$

The blackness of the solution should be accepted as an empirical observation of a solution property. The value reports on the net effect of competition between hydrogenation, depolymerization, and repolymerization reactions. It is one of the most sensitive indexes which can be used to investigate the state of the product solution from the reactor. Normally blackness increases as the concentration of coal in the feed is increased. Factors which increase the amount of hydrogen which is reacting tend to reduce the blackness of the solution while increased temperature-time stress on the system usually will cause an increase in the blackness of the solution. The responses are non linear and have not been fitted into a quantitative discussion despite the considerable reproducibility of the blackness observations. The blackness determination requires only a few drops of solution and can be completed in a few minutes time. The combined information from $\overline{IR}$ and blackness determinations therefore provides supporting indications related to the course of the reaction and its probable extent of conversion. Also, it is readily determined if the same product is being obtained from sample to sample by use of these methods. Such results are available in a fraction of the time needed for an evaluation based on solution workup by distillation.

Gas analyses are also of value in monitoring the reaction. Concentrations of output gases including hydrocarbons, CO_2, CO, H_2S, and small amounts of ammonia are determined by standard means including infrared spectra, molecular weight, gas solid chromatography, and volumetric determination of the hydrogen sulfide. Unreacted hydrogen is calculated from the composition and volume of the output gas. This is subtracted from the hydrogen input to calculate the amount of hydrogen reacted. The yield of hydrogen sulfide in the output gas is a good indication of the amount of desulfurization which is observed, although enough sulfide is dissolved in the water to cause some nonlinearity in this observation also. This is because the water dissolves ammonia which extracts both carbon dioxide and hydrogen sulfide from the gases until the ammonia is neutralized.

The above analyses are used in monitoring the continuous operation of the reactors. After product workup and solvent isolation, more detailed analyses of products are carried out. Recycle solvents are analyzed by infrared, nuclear magnetic resonance, and elemental and physical analysis methods. For Solvent Refined Coal Product the elemental analysis, percentage ash, and the fusion point are determined. Product distribution is determined by performing all distillations and filtrations quantitatively. The insoluble residue is carefully pyridine washed and the MAF conversion of the coal is calculated from the relative proportions of ash and carbonaceous matter in the insoluble residue after careful drying of the washed residue. Liquid products may be further characterized by density determinations and by functional group analysis such as titration of amine or phenolic functions. These functions also tend to establish characteristic concentrations in the recycle solvent, for example, and provide additional inspection methods for lineout.

E. Range of Conditions Explored in These Experiments

The operating conditions and related information for the experiments under discussion are summarized in Table III. In this table each experiment is numbered and represents a continuous operation from a single startup of the reactor. A change in operating conditions is given a letter code and implies a lineout at a new condition.

F. Discussion of Experimental Results

Results of runs with the two vessel reactor system are presented for comparison purposes. The first of these, Run CU 77, may be considered as a base run from which modifications were made; first to simulate startup conditions at the Ft. Lewis pilot plant, and then modified to improve desulfurization, solvent recovery, and the reactivity of the recycle solvent for better long term operation.

Run CU 77 was the eleventh pass of solvent in a series, described earlier, designed to simulate startup of the Ft. Lewis pilot plant with a petroleum derived solvent. 9/
This series of experiments was started with FS 120 Carbon Black Feedstock and was designed to recycle the solvent recovered from pass to pass until an equilibrated

recycle solvent had been developed. From recent work it is now established that the eleventh pass solvent was not completely free of the influence of the startup solvent. The concentration of sulfur in the eleventh pass solvent was higher than the level observed in later equilibration products due to the presence of a fraction of stable sulfur containing compounds in FS 120. However, the bulk of the solvent hydrocarbon materials appears to have been equilibrated fairly well.

The CU 77 product distribution and SRC Product analysis are shown in Figure 2 and Table IV, respectively. A recycle solvent cut of 100-250°C at 3 mm Hg provided a 99% return of solvent in this experiment. A break-even solvent yield could be accomplished by addition of part of the cut 1 oil obtained. No attempt was made to optimize desulfurization in this series of experiments; vacuum bottoms contained 1.0% sulfur. The feed coal for CU 77 contained 1.50% organic sulfur which is somewhat higher than the 1.29% organic sulfur reported in Table I for the Kentucky No. 9 coal used in later experiments. This could be due to a mine run variation in composition or to the inclusion of some Kentucky No. 14 coal in the sample.

The next runs to be considered were made on the same equipment but operating conditions were changed to match the proposed startup conditions for the Ft. Lewis Pilot Plant. The initial solvent used was a blend of FS 120, crude anthracene oil, and some creosote oil. The laboratory operating procedure was modified by distilling the unfiltered product solution to recover solvent for recycle; this expedites attainment of equilibrated recycle solvent. Because the FS 120 component of the solvent was known to be low in reactivity, operating temperature for run CU 89 was 425°C in both the preheater and dissolver for the first few cycles; the temperature was then advanced in stages when the composition of the solvent had changed enough to justify a change in operating conditions. Final operating temperature was 445°C in both the preheater and dissolver. A plot showing the course of the $\overline{IR}$ and blackness functions for this experiment is presented as Figure 3. This plot also indicates the solvent recovery as a function of sample number in the experiment.

A gradual decline in hydrogen in the product solution is indicated by the $\overline{IR}$ function. Initial solvent recovery was low because of a high molecular weight fraction in the FS 120 which would not be distilled at the final temperature of the solvent reclaim distillation. Solvent recovery then improved rapidly but lined out at only 96% return on the average. Use of all available cut 1 oil would have allowed break-even operation. The operation could have been improved by the use of a higher distillation endpoint but distillations were finished near the temperature at which decomposition was a factor. The experiment was continued with the same solvent after a new startup (hence the designation experiment CU 90). By this time the Ft. Lewis Pilot Plant had been operated and an exotherm in the dissolver had been observed to raise the reactor to an average temperature of about 450°C with the preheater at 425°C. Experiment CU 90 was therefore initiated at a preheater temperature of 425°C and a dissolver temperature of 450°C. This experiment was conducted with great difficulty; flow through the reactor was interrupted by repeated plugging of the preheater. Somewhat better operation was achieved at a preheater temperature of 440°C rather than the planned 425°C but plugging was still severe. From the number of plugs encountered and subsequent inspection of the equipment it appeared that the solvent obtained in the CU 89 experiment had been insufficiently reactive and that a slow deposition of carbon in the preheater had been in effect during the latter stages of the CU 89 experiment. This spalled off the tube later when the new startup was attempted and carbon deposition caused plugs to form at constrictions in fittings. This appears to be the main problem in recycling of a solvent which has not been well hydrogenated, since the slurry will tolerate only mild and carefully controlled heating in this circumstance. The uniformity of heating the preheater by the fluidized sand bath may not be sufficiently good for work near critical temperature limits, and this may have been a contributing factor in the difficulties observed. In any case the use of a high final temperature for desulfurization of product does not appear to be good procedure. The vacuum bottoms products which were made in experiment CU 89 contained an average of 0.83% of sulfur and in CU 90 the vacuum bottoms contained an average of 0.75% of sulfur. Thus use of hot reaction conditions had been effective in removal of sulfur, but at the cost of preparing a solvent of doubtful stability and reactivity on recycle. The concentration of coal was increased in experiment CU 90 to 30%. This may have been another factor in producing a less stable solution in the hot reactor but the concentration of coal is not thought to be the main problem.

It had been previously established that good performance in a coal dissolver could be obtained if the preheater were operated at a comparatively high temperature (450^{o}C to 460^{o}C for example) while the dissolver was operated at a milder temperature (about 425^{o}C for example). This two temperature - two vessel system had been used routinely in the laboratory with good results. Experiment CU 77 typifies application of this strategy. In initial trials in the Ft. Lewis Pilot Plant it was found that the first dissolver heated spontaneously, as the result of the exothermic heat of hydrogenation, to a temperature of about 450^{o}C. This is higher than the preferred final reactor temperature for preparation of a well hydrogenated recycle solvent. The preheater was operated at a maximum temperature of 425^{o}C in order to minimize the temperature in the first dissolver. As a consequence the actual operation of the preheater and dissolver was not in the preferred temperature profile and not in the profile which had been used in most of the lineout study program done in the laboratory. Sulfur removal using this temperature profile had been good, resulting from exposure of the product solution to heat for relatively long time intervals. The problem therefore appeared to reduce to the question of obtaining and using good temperature controls in the reactors at hand. The Ft. Lewis Pilot Plant installation includes a second dissolver which can be operated in series with the first. It was therefore reasonable to investigate configurations in which the preheater temperature was mild (425^{o}C), the first dissolver was allowed to heat under the influence of the exothermic reaction, and the last dissolver was presumed to be cooled to produce a solvent with a better hydrogen concentration in it. Such final temperatures were expected to fall in the 400^{o}C to 425^{o}C range with the best temperature not established. Experiments of this kind were simulated in runs CU 91 through CU 93.

Use of the second dissolver could be simulated in the laboratory by changing the location of the dip tube in the two liter autoclave to allow a volume of liquid product to accumulate in this vessel. In order to have a reaction in the autoclave it was necessary to heat it to normal reaction temperatures. Since a new heater and new equipment operations were involved it was decided to explore the use of the lower operating temperatures in the range of interest first. The autoclave has therefore been used only at 400^{o}C in trials to be reported.

The initial investigation with the modified reactor system was done using the conditions shown for experiment CU 91A. The study was started with an initial solvent charge of lightly hydrogenated anthracene oil. As solvent was recycled in the process the concentration of hydrogen in the solution and in the reclaimed solvent was observed to increase. This was followed by means of infrared spectra for product solution and the reclaimed solvent. The course of the $\overline{\text{IR}}$, blackness, and solvent recovery functions for this experiment is shown in Figure 4. In the initial series of samples made the recovery of solvent was improved for this operating mode. It was also observed that over half of the hydrogen added to the reactor was consumed. It was obvious that not as much hydrogen was being added as could be reacted under these conditions. The hydrogen flow rate was therefore increased without collecting a sample to represent the initial hydrogen starved portion of the experiment. The second portion of the experiment, after increasing the hydrogen flow, was designated experiment CU 91B.

The increased hydrogen addition rate caused an abrupt decline in the blackness of the solution and an abrupt increase in the $\overline{\text{IR}}$ values for the coal solution and for the reclaimed solvent obtained by redistillation of the coal solution. The increase in reacted hydrogen was confirmed by subsequent analysis for samples of the reclaimed solvent. The experiment was continued for a total of thirty samples, with return of the reclaimed solvent to the feed slurry in each case, in an effort to equilibrate the solvent as well as possible. Finally most of the feed slurry was run through the reactors to make two samples of solution for workup by filtration and preparation of the usual ash-free vacuum bottoms and reclaim solvent samples. Samples were analyzed. The reclaimed solvent was pooled for use in experiment CU 92. Vacuum bottoms properties are given in Table IV and reclaim solvent properties are given in Table V.

Observation of abrupt changes in the composition of these products in response to changes in the hydrogen input rate is convincing evidence that the material in the reactors is effectively catalyzed. Given suitable temperatures and hydrogen pressures, the coal can be reduced by hydrogen, and production of liquified material which accounts for most of the organic matter in the coal is possible. The MAF conversion in this case was 97.3% for the average of the two final samples in the series. Another convincing observation is the comparatively low sulfur content of the vacuum bottoms samples. In this case the vacuum bottoms contained 0.52% to 0.56% of sulfur.

The lightly hydrogenated anthracene oil which was used as the initial charge of solvent in this experiment contained 6.04% hydrogen. In the hydrogen starved portion of the experiment the reclaimed solvent had remained at substantially this composition. The analysis for several reclaim solvent samples is presented in Table V and it can be seen that the solvent had remained close to the composition of the initial solvent charge through sample 12. Sample 11 contained 6.00% hydrogen for example. Values for $\overline{\text{IR}}$ for the solution also indicate little change in the composition of the solution during this portion of the experiment. After the hydrogen flow was increased the $\overline{\text{IR}}$ values for solution samples and for the reclaimed solvent increased. The hydrogen content of the 14th sample increased to 6.58% for example. This composition remained established throughout the remaining samples with minor variations only. It should be remarked that $\overline{\text{IR}}$ values for the coal solutions contain a component contributed by the dissolved coal, and that the reclaimed solvent commonly will yield a different value. The volume of slurry required to maintain a safe level of material in the feed system while solutions were being redistilled to obtain reclaim solvent was such that about 3 or 4 samples were needed to complete one pass of solvent through the reactor system. Experiment CU 91 therefore represents about 6 or 7 passes of solvent through the reactor.

Experiment CU 92 was started with the slurry heel retained from the previous experiment plus additional slurry formulated with the solvent reclaimed from the final samples prepared and worked up for analysis. In this sense experiment CU 92 is a continuation of the previous experiment. The initial operating temperatures were also the same as the final temperatures used in the previous experiment. The concentration of coal was increased from 30% used in the previous experiment to 35%. This change combined with a small adjustment in the hydrogen input rate resulted in reducing the hydrogen input rate from 8.0% in the CU 91B experiment to 5.6% based on the feed coal in the latter case. The CU 92A portion of the experiment was continued for 13 samples and an hour long sample was then taken for complete workup. After this sample was completed the temperature of the first dissolver was reduced from 450°C to 435°C.

This change resulted in an abrupt decline in the blackness of the solution and again a sharp increase in the IR values of the product solution and of the reclaimed solvent obtained from the solution. In addition a small exothermic reaction developed in the second dissolver which caused the temperature to increase from 400°C to the vicinity of 410°C. This persisted until the controller for the outer jacket was reset to allow a cooler jacket temperature. During this time the yield of solvent was well above the break-even amount. This situation prevailed throughout the remaining part of the experiment and would have averaged about 4% excess assuming the cut 1 oil were formulated also. The reactivity of the system appeared to oscillate throughout the remainder of the experiment.

The vacuum bottoms sample taken at the end of the CU 92A sequence contained only 0.54% sulfur. The samples taken at the end of the CU 92B sequence contained sulfur ranging from 0.60% to 0.70% and the values seemed to be under the influence of reactor oscillation. The reclaimed solvent obtained in the CU 92A sequence contained 6.64% hydrogen (from sample 14) while the reclaimed solvent made in the CU 92B part of the experiment contained an average of about 6.85% hydrogen. The control functions, IR and blackness, therefore reported this trend with apparent reliability. During this portion of the experiment the solvent accumulated another 6 or 7 cycles of use. Data for CU 92 are plotted in Figure 5.

Experiment CU 93 continued with the recycled solvent recovered from the previous experiment. The initial slurry contained 35% coal; operating changes were a reduction of the first dissolver from 435° to 425°C and an increase in the preheater from 425° to 450°C. This portion of the experiment was run with some difficulty since the temperature recorder failed at the end of the 5th sample. The continuous operation was sustained by moving a portable potentiometer from one thermocouple to another while the multipoint recorder was being repaired. Temperature control was upset during several samples and blackness, IR values, and the amount of recycle solvent obtained all show related effects during this portion of the experiment. The upset seemed to be well corrected by the 14th sample. A sample was therefore collected for complete workup at this time. The concentration of coal in the feed slurry was then increased to 40% to continue with the CU 93B sequence. This change resulted in an increase in the blackness of the solution but did not result in much effect on the IR values for the coal solution. Oscillation of the amount of reclaim solvent available for recycle developed following the increase in coal concentration. Experiment CU 93 included the attempt to crowd three experiments into a week of continuous operation. A sample was taken to represent the equilibrated product at the 23rd sample. The temperature of the first dissolver was then increased to the 435°C level to investigate the prospect for better sulfur removal at this temperature. This change resulted in an increase in the blackness of the solution, little effect on the IR values for the coal solution, and a temporary drop in the amount of solvent which could be reclaimed from the unfiltered coal solution. This drop appears to have been mostly corrected five samples after the temperature change. Samples 29, 30, and 31 were taken for complete workup and analysis. It is questionable whether stable operation had been established at the time the reactor was shut down. The trend appeared established for a small yield of excess solvent in the usual solvent range, with some additional cut 1 oil available if needed. The vacuum bottoms sample representing CU 93A operations contained 0.59% sulfur. The vacuum bottoms representing CU 93B operations contained 0.73% sulfur. The experiment was terminated by the preparation of three samples for complete workup. The vacuum bottoms representing the CU 93C condition contained sulfur ranging from 0.62% to 0.69%. Data for CU 93 are plotted in Figure 6.

G. Reporting of Yield and Sulfur Balance Results

Methods have been developed for measuring the inputs and outputs in experiments in this continuous reactor system with precision. These are reported in detail in OCR Report 53, Interim Report 8. As a result of these studies material balances are commonly closed to account for 99.5% of the materials in each of the samples made. Distillations and filtrations are managed in a quantitative procedure which normally accounts for better than 99% of the materials in these subsidiary operations. Usually these results are summarized in the form of a yield table and a flow chart which consolidates several samples in a single average calculation. An example of such data is presented as Figure 7 which gives the detailed summary for experiment CU 92B and which reports the data based on three samples collected at the end of that experiment for complete analysis. The information on this chart can be combined with elemental analysis results to calculate the balance of sulfur in the process. The balance is presented in Table VI. Sulfur balance was closed with good accuracy. Sulfur is removed by the evolution of hydrogen sulfide and with the mineral phases removed by filtration. A small amount of sulfur is removed as ammonium sulfide dissolved in the water produced.

III SUMMARY

Measurements useful in studying the Solvent Refined Coal continuous reactor have been described. Several changes in operating conditions have been investigated with recycle of solvent at each condition so that the recycle solvent is in equilibrium with the process. Addition of a second dissolver vessel which is operated at a lower temperature than the preheater and the first dissolver had the following beneficial effects.

1. Improved desulfurization
2. Increased solvent recovery
3. Improved hydrogen transfer capacity of the recycle solvent.

Coal concentrations up to 40% in the feed slurry have been used without difficulty. Solvent Refined Coal Products with sulfur levels as low as 0.52% have been obtained. Conditions used are not known to be optimal but the stepwise investigation of variables described has brought about significant improvement in the sulfur content of the vacuum bottoms product.

Table I

Analysis of First Lot Pilot Plant Coal

Sample: First lot coal for Ft. Lewis Pilot Plant
Six car composite; received May 7, 1974
From Colonial Mine, Hopkins County, Kentucky

PROXIMATE ANALYSIS	As received	Dry basis
% Moisture	5.84	xxxxx
% Ash	7.95	8.44
% Volatile	39.89	42.36
% Fixed Carbon	46.32	49.20
	100.00	100.00
Btu	12529	13306
% Sulfur	3.14	3.33
% Alk as Na_2O	xxxxx	0.12
SULFUR FORMS		
% Pyritic Sulfur	1.87	1.99
% Sulfate Sulfur	0.05	0.05
% Organic Sulfur	1.22	1.29
% Total Sulfur	3.14	3.33

ULTIMATE ANALYSIS	% Weight As received	Dry basis
Moisture	5.84	xxxxx
Carbon	69.15	73.44
Hydrogen	4.99	5.30
Nitrogen	1.53	1.62
Chlorine	0.02	0.02
Sulfur	3.14	3.33
Ash	7.95	8.44
Oxygen (diff)	7.38	7.85
	100.00	100.00

MINERAL ANALYSIS	% Weight
Phos.pentoxide,P_2O_5	0.22
Silica, SiO_2	40.18
Ferric oxide,Fe_2O_3	31.28
Alumina,Al_2O_3	22.00
Titania,TiO_2	0.98
Lime,CaO	1.60
Magnesia,MgO	0.65
Sulfur trioxide,SO_3	0.55
Potassium oxide,K_2O	1.88
Sodium oxide,Na_2O	0.23
Undetermined	0.43
	100.00

FREE SWELLING INDEX = 4
SILICA VALUE = 54.51
T250 = 2260°F

Table II

Composition of Initial Solvents Used

Solvent	FS 120 Carbon Black Feedstock	CU40 Hydrogenated Anthracene Oil	Ft. Lewis Solvent Blend
Carbon	89.52	90.58	90.28
Hydrogen	7.72	6.04	6.76
Nitrogen		1.07	
Sulfur	2.20	0.36	1.62
Oxygen		1.95	
IR Value	4.47	0.98	1.81
Proton Distribution % by NMR*			
H_γ (30-60 Hz)	9.2	1.6	4.5
H_β (60-120 Hz)	31.4	8.6	14.7
H_α (120-200 Hz)	29.7	20.5	26.6
H_{Ar} (360-512 Hz)	29.7	69.3	54.2

* See reference 9

Table IV

Composition of Vacuum Bottoms

Experiment	Sample #	% C	% H	% S	% Ash	MP^{o}C
CU 77	Average	87.88	5.33	1.03	0.079	207
CU 89	19	87.59	5.37	0.84	0.046	180
	20	87.77	5.46	0.83	0.058	198
CU 90	8	89.21	5.09	0.75	0.075	219
CU 91B	31	89.29	5.70	0.52	0.11	171
	32			0.56	0.16	226
CU 92A	14	88.19	5.16	0.54	0.11	223
CU 92B	31	87.84	5.43	0.60	0.10	212
	32	87.55	5.52	0.70	0.09	215
	33	86.83	5.11	0.64	0.11	220
CU 93A				0.59	0.21	243
93B		87.59	5.38	0.73	0.10	238
93C	29	88.24	5.34	0.69	0.10	225
	30	87.80	5.30	0.68	0.19	225
	31	88.09	5.22	0.62	0.11	235

Table III

Range of Conditions Explored

Run	Press. psig	Temperatures, °C			Coal Concentration in Slurry %	Feed Rates			Hydrogen Feed Wgt. % Based on Coal
		Preheater	1st Dissolver	2nd Dissolver		g slurry/ hr.	lbs.slurry hr./cu.ft.[a]	lbs.coal/ hr./cu.ft[a]	
CU 77	1500	455	435	-	36	520	57.9	20.8	6.4
CU 89	↓	425→445	425→445	-	25	610	68.0	17.0	4.9
CU 90	↓	440	450	-	30	520	57.9	17.4	4.9
CU 91A	↓	425	450	400	30	800	44.4	13.3	4.2
CU 91B	↓	425	450	400	30	800	44.4	13.3	8.0
CU 92A	↓	425	450	400	35	800	44.4	15.5	5.6
CU 92B	↓	425	435	400	35	800	44.4	15.5	5.6
CU 93A	↓	450	425	400	35	800	44.4	15.5	5.4
CU 93B	↓	450	425	400	40	800	44.4	17.8	4.8
CU 93C	↓	450	435	400	40	800	44.4	17.8	4.8

a) Includes combined volume of preheater and dissolver(s).

Table V

Properties of Recycle Solvents

Experiment	Sample #	% C	% H	% S	Density	$\overline{IR}$ in CS_2 Solution	Proton Distribution by NMR* H_γ 30-60	H_β 60-120	H_α 120-200	H_{Ar} 360-512
Started with FS 120										
CU 77	Average	88.66	6.99	1.98	1.071	2.19	4.9	18.3	28.9	48.0
Started with Ft. Lewis startup solvent blend										
CU 89	19	89.83	6.77	1.24	1.085	1.74	2.4	11.8	25.9	59.9
	20	89.79	6.54	1.31	1.087	1.30	2.1	10.5	25.3	62.1
CU 90	7	89.75	6.58	1.18	1.086	1.21	2.0	11.1	25.3	61.6
Started with partly hydrogenated anthracene oil										
CU 91A	7	90.40	6.08	0.41		0.92	1.3	8.8	21.7	68.7
	9	90.56	6.05		1.107					
	11	90.43	6.00	0.39	1.102	0.95	1.5	8.9	21.2	68.2
CU 91B	14	90.53	6.58	0.41	---	1.20	1.5	11.3	23.1	64.1
	30	89.63	6.57	0.41	---	1.40	2.4	13.0	24.5	60.1
	31	---	---	0.38	---	1.35	2.1	12.4	24.2	61.3
	32	89.65	6.68	0.42	1.092	1.45	2.2	13.2	24.9	59.7
CU 92A	14	89.59	6.64	0.51	1.093	1.45	2.3	14.2	25.3	58.2
CU 92B	31	89.05	6.82	0.51	---	1.8[illegible]	2.7	15.1	27.4	54.8
	32	89.03	6.85	0.51	1.085	1.76	3.8	16.1	26.5	53.5
	33	---	---	0.49	---	1.74	3.3	16.0	27.2	53.5
CU 93A	A	88.34	7.18	0.48	1.091	1.95	2.4	16.3	28.4	52.4
CU 93B	B	88.51	6.98	0.49	1.076	2.13	3.3	17.3	29.9	49.5
CU 93C	29	88.30	7.22	0.48		2.10	5.0	17.3	28.2	49.5
	30	88.40	7.08	0.51	1.070	2.14	4.5	17.8	28.2	49.5
	31	88.03	7.17	0.49		2.17	4.6	17.9	28.3	49.2

* See reference 9

Table VI

Sulfur Balance Data for Run CU 92B
Composite samples 31, 32, & 33
Yields from Figure 7

Substance	Weight Grams	% Sulfur	Grams S
Input			
Coal	2527	3.33	84.15
Solvent	4649	0.49	22.78
Hydrogen	141		
Total	7317		106.93
Output			
Gas (raw)[a]	366		36.62
Water (Composite)	187.1	0.92	1.72
Cold Trap Oil	59.2	0.76	0.45
Cut 1 Oil	194.3	0.42	0.81
Cut 2 Oil	4607	0.50	23.03
Vacuum Bottoms	1514	0.65	9.84
Pyridine Insolubles	376.3	9.29	34.96
Not accounted for	12.7		
Total	7316.6		107.43
Accountability			100.5%

a) Gas output = 42.39 moles at 2.70 mol % hydrogen sulfide. This accounts for 36.62 grams of sulfur.

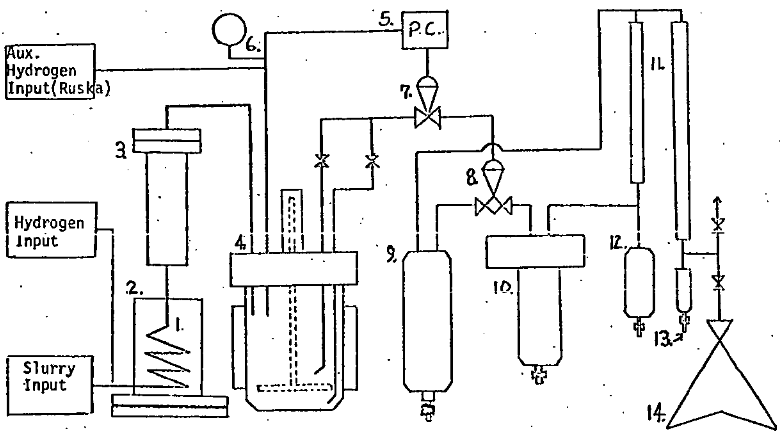
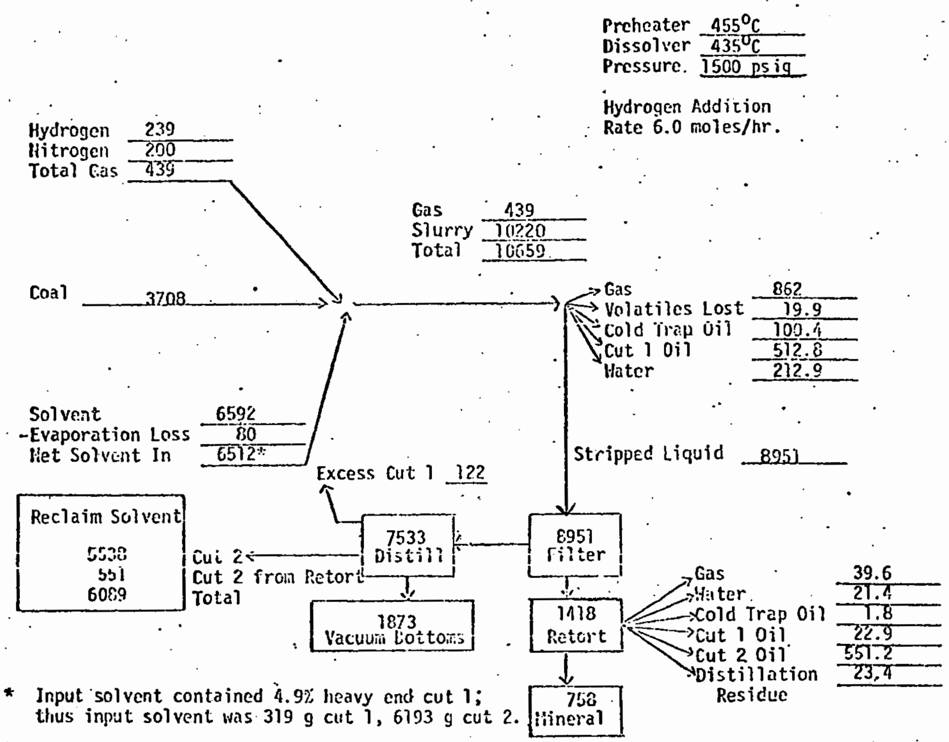


Figure 1. Simplified Schematic Continuous Reactor
(Not to scale)

Legend
1. Preheater Coil
2. Fluidized Sand Bath
3. 1st Dissolver (450ml Autoclave)
4. 2nd Dissolver (2 liter Autoclave, Volume used ca 565 ml)
5. Pressure Controller
6. Reactor Pressure Indicator
7. Gismo Valve
8. 3-Way Manifold Valve
9. Slop Vessel
10. Flash Vessel
11. Cold water condensers
12. Flash Condensate Receiver
13. Knockout Vessel
14. Gas Collection Bag

Figure 2 CU 77 Flow Diagram
11th Pass of Reclaim Solvent



* Input solvent contained 4.9% heavy end cut 1; thus input solvent was 319 g cut 1, 6193 g cut 2.

PRODUCT SUMMARY		Weight	% of Feed Slurry	% of Raw Coal
Gas	902			
H_2	-161			
N_2	-200			
Net Gas		541	5.29	14.58
Water		234.3	2.29	6.31
Volatiles Lost		19.9	0.19	0.52
Cold Trap Oil		102.2	1.00	2.76
Cut 1 Oil		657.7[a]	6.44-3.12[c]-1.02[d]	6.34
Cut 2 Oil		6089.2	59.58+3.12[c]+1.02[d]	-
Heavy Residue (Retort)		23.4	0.23	0.63
Vacuum Bottoms		1873	18.33	50.52
Dry Mineral		758	7.42	20.45
			100.77%[b]	102.11[b]

a Includes excess cut 1 oil from distillation.
b Greater than 100% due to addition of hydrogen.
c Cut 1 oil in input slurry.
d Additional cut 1 oil needed to reach breakeven reclaim solvent yield of 63.72%.

Figure 3 Data Plots Run CU 89

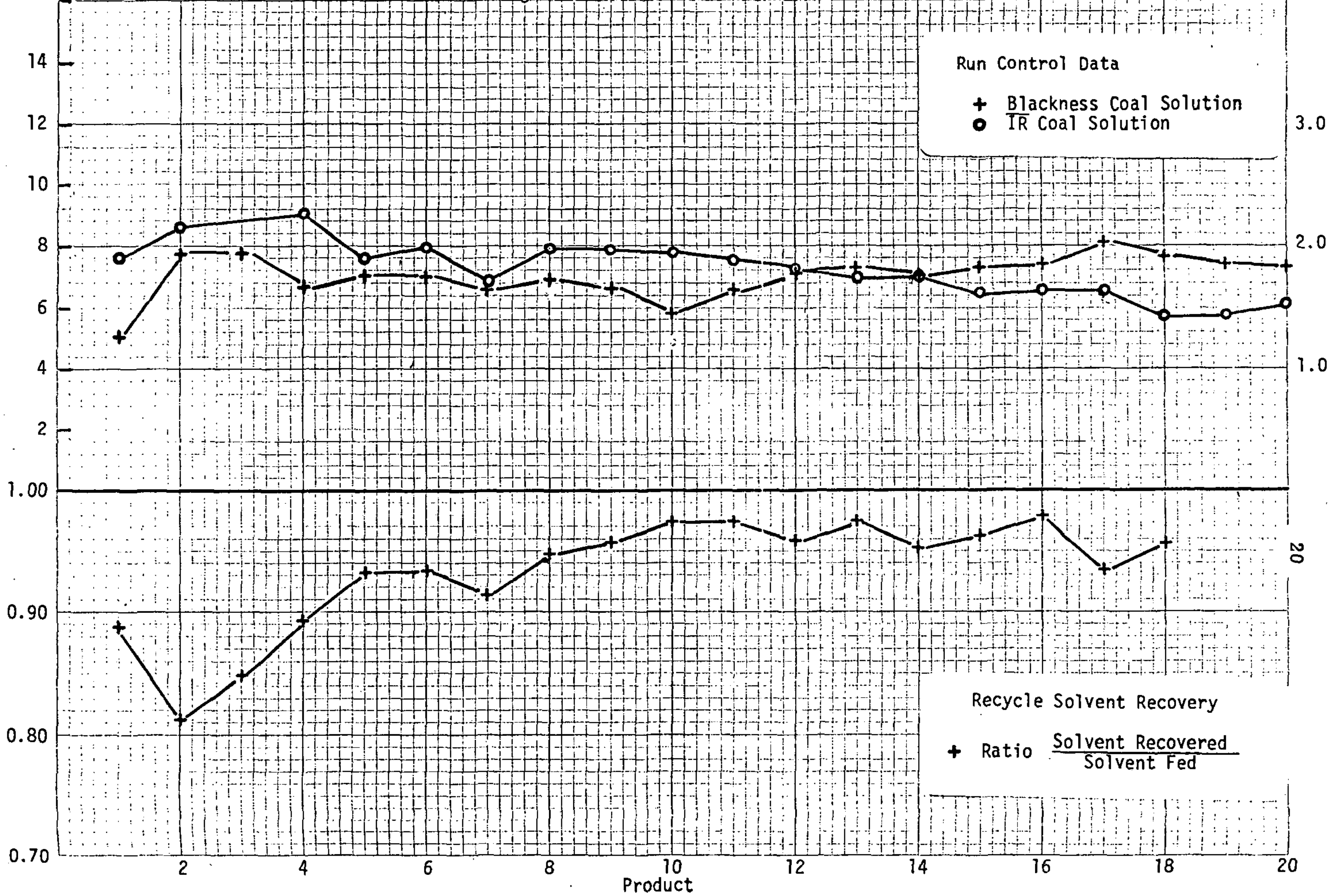


Figure 4 Data Plots Run CU 91

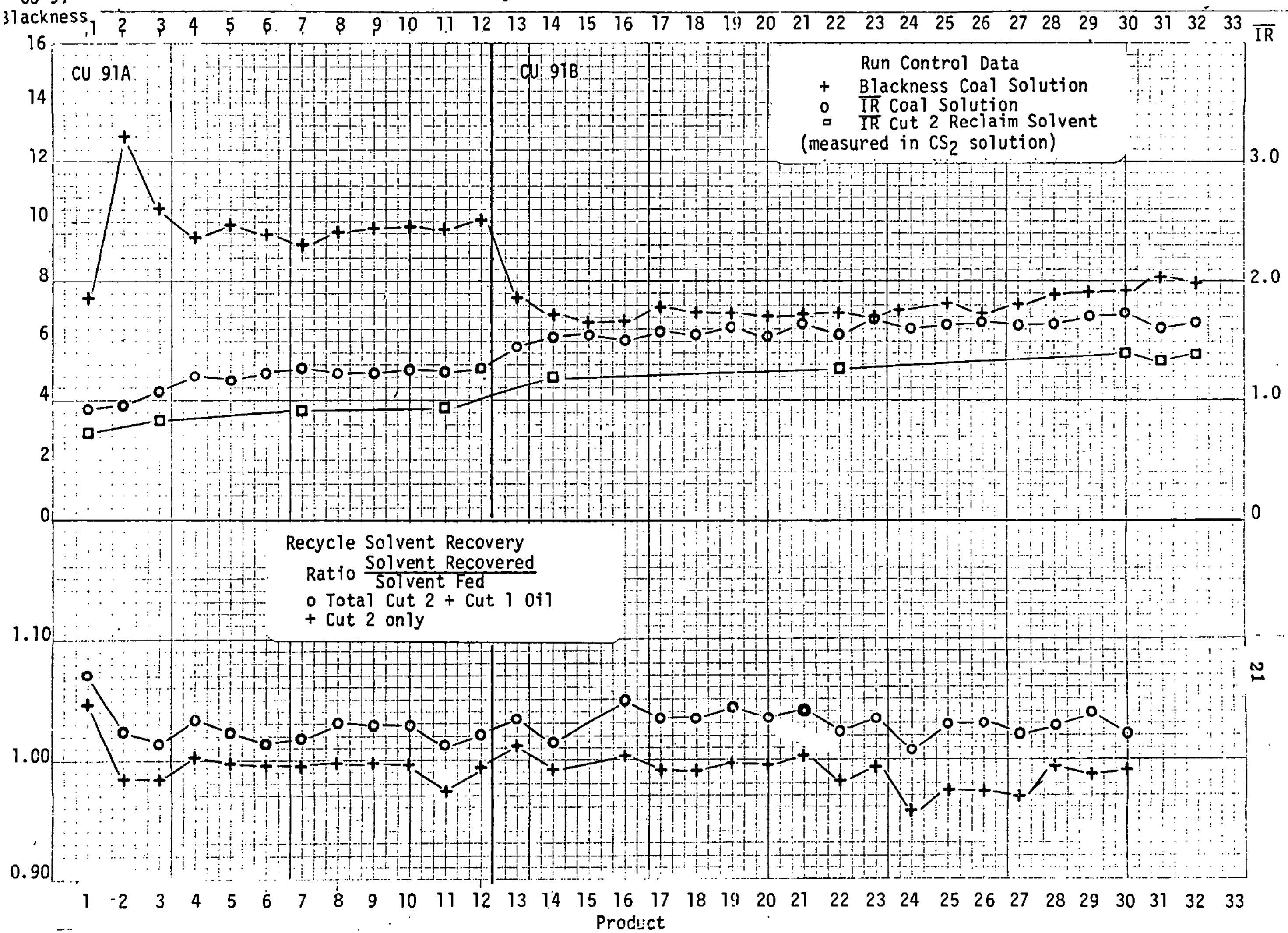


Figure 5 Data Plots Run CU 92

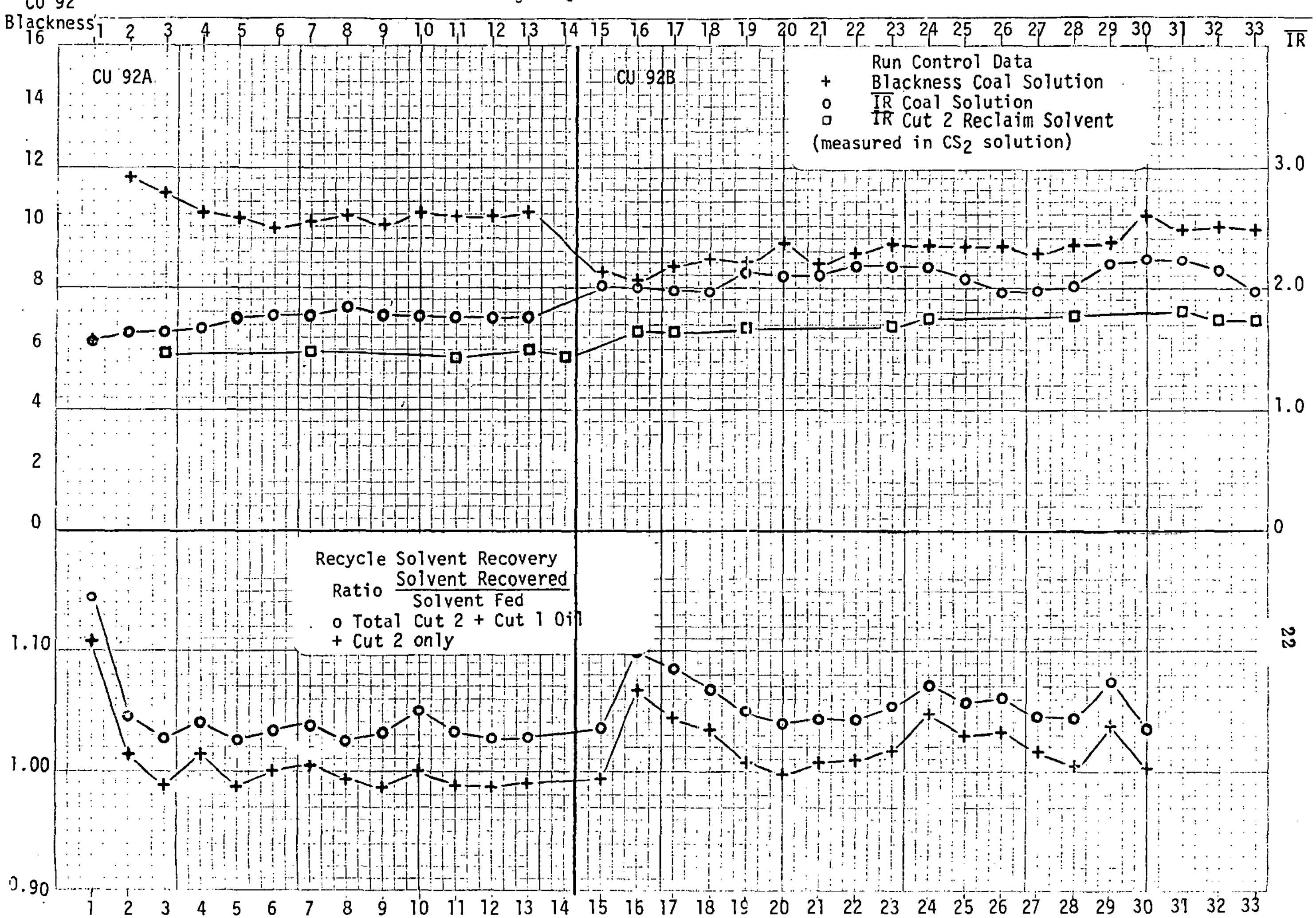


Figure 6 Data Plots Run CU 93

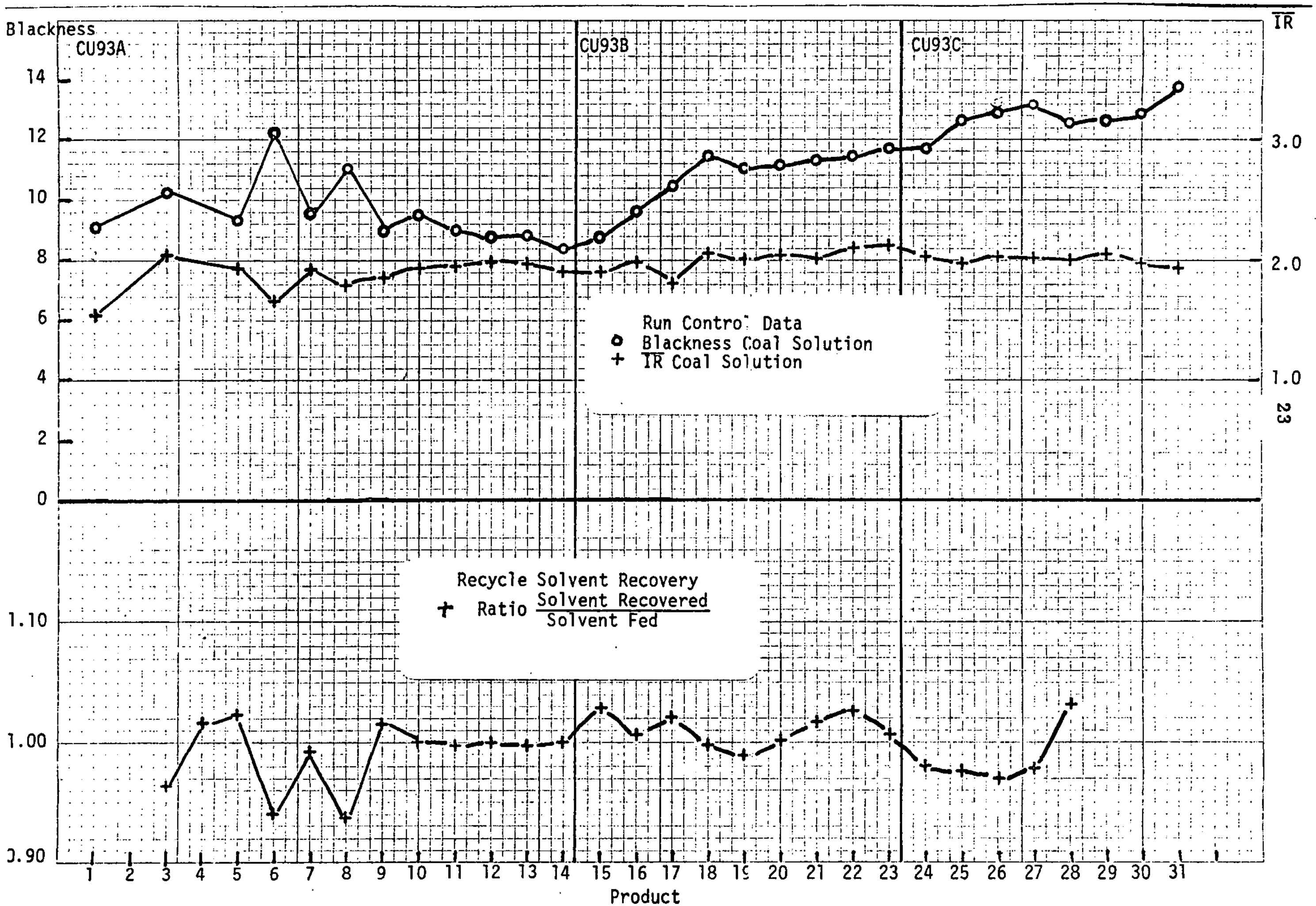
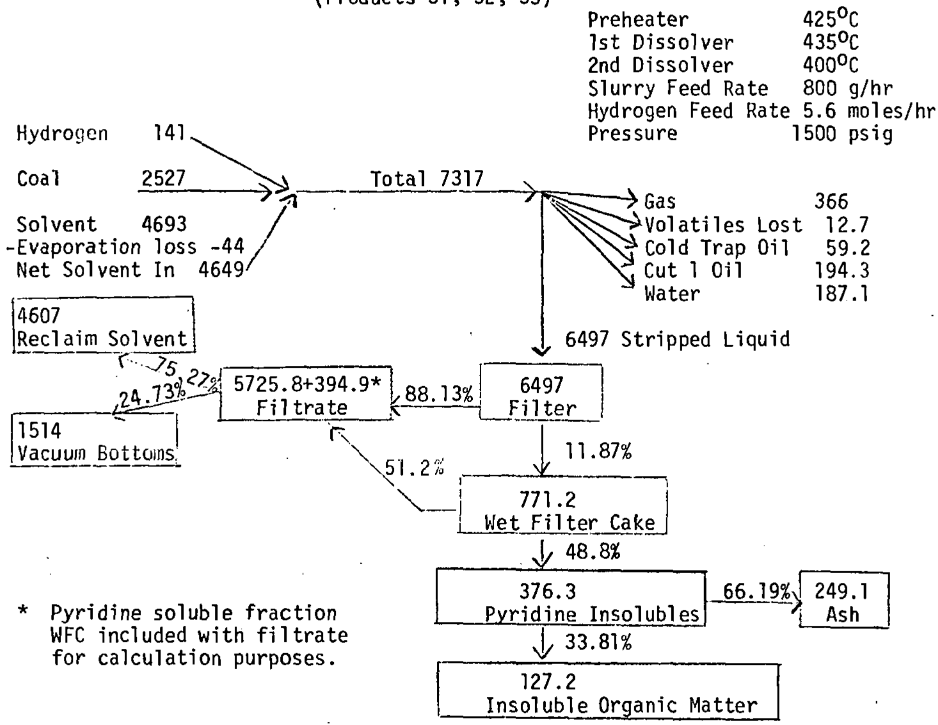


Figure 7 CU 92B Flow Diagram
(Products 31, 32, 33)



* Pyridine soluble fraction WFC included with filtrate for calculation purposes.

Product Summary	Weight	% of Feed Slurry	% of Raw Coal
Total Gas 366			
H_2 - 87			
Net Gas	279	3.89	11.05
Water	187.1	2.61	7.41
Volatiles Lost	12.7	0.18	0.51
Cold Trap Oil	59.2	0.82	2.33
Cut 1 Oil	194.3	2.71 - 0.59[b]	6.02
Cut 2 Oil	4607	64.20[a] + 0.59[b]	-
Vacuum Bottoms	1514	21.10	59.92
Ash	249.1	3.47	9.85
Insoluble Organic Matter	127.2	1.78	5.05
Total		100.76	102.14

a) Correct input cut 2 concentration is 64.79%.
b) Amount of cut 1 required to reach breakeven solvent yield.

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CO-STEAM COAL LIQUEFACTION IN A BATCH REACTOR

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ABSTRACT

The CO-steam process of coal liquefaction was studied at the Colorado School of Mines to determine the effects of temperature and pressure on the liquefaction and desulfurization of a high sulfur bituminous coal. The CO-steam process utilizes the shift reaction, which reacts water and carbon monoxide to form hydrogen and carbon dioxide, as the source of hydrogen for hydrogenation and desulfurization of the coal. The coal was dissolved with a creosote oil solvent before reaction.

Experimentation was done in batch autoclave reactors. Reaction temperatures were varied from 375°C to 475°C and reaction pressures were varied from 2500 psig to 3500 psig by varying the initial carbon monoxide pressure at room temperature from 400 psig to 600 psig. Fixed operating variables were: solvent-to-coal ratio, water-to-coal ratio, reaction time, and solvent type. The following analyses were performed on the liquid coal and solvent mixture: percent benzene insolubles, total sulfur analysis, kinematic viscosity, carbon hydrogen analysis, reaction gas analysis, and heating values. Sulfur balances and overall material balances were calculated.

The results indicate that conversion of coal to liquid increases with an increase in reaction temperature over the range studied. However, changes in carbon monoxide pressures did not appear to have any definite effect on coal conversion in the pressure range investigated. Coal conversions ranged from 57 to 99 percent on a moisture and ash-free basis.

Coal desulfurization increased with an increase in reaction temperature over the range studied. Desulfurization results found in this study were not as good as those potentially attainable using pure hydrogen. The maximum desulfurization attained in this study was 57 percent. The desulfurization obtained may not be the maximum attainable under the reaction conditions studied because of the equilibrium limitations of a batch reactor.

INTRODUCTION

Now, because of the energy shortage, pollution controls and dependence on foreign oil sources, there is a growing interest in coal liquefaction to produce a clean fuel oil from domestic resources. Many power plants burn fuel oil and natural gas instead of coal to meet environmental pollution regulations. If a coal-derived oil were used to replace the current feeds to power plants this would release the petroleum oils and gas consumed by power plants for use in home heating, industry, and motor fuel, thus relieving the shortage of petroleum-derived fuels. Conversion of coal to clean fuels can be accomplished both by liquefaction and gasification; however, the liquefaction conversion has a higher thermal efficiency. In addition, the liquid fuel produced in liquefaction has a higher energy density than gaseous fuels and therefore is cheaper to transport and store.

Converting coal to a liquid generally requires the addition of hydrogen. If the hydrogen content of the coal is increased by 2 to 3 percent, mild liquefaction results. The heavy oil produced under mild liquefaction conditions can be used as feed to electric power boiler generators. If the hydrogen content of the coal is increased by 6 percent or more, light oils and gasoline are produced. If the liquefied coal is to be used as a boiler feed a heavy oil is preferred because it is less costly to produce due to less hydrogen consumption (1) and it has a higher energy density (2). In addition the heavy oil product may be used as a low-sulfur utility fuel either directly or after further refinement by removal of the ash and unreacted coal. Its use would depend on the design of the furnace to be fired with the synthetic liquid fuel.

Hydrogen is a very expensive raw material; therefore, liquefaction of coal using hydrogen directly would be a costly process. A way around this problem is to produce the hydrogen needed for the liquefaction of coal from less expensive raw materials. This can be accomplished using the water-gas shift reaction. In this reaction water and carbon monoxide react to form hydrogen and carbon dioxide and both starting materials, water and carbon monoxide, are inexpensive and readily available.

The source of hydrogen used in liquefying the coal in the CO-steam process comes from the reaction of carbon monoxide and water to form hydrogen and carbon dioxide. The interaction of carbon monoxide and water with coal is not as simple as the interaction of pure hydrogen and coal (6). Carbon monoxide and water have been found to liquefy coal more completely than pure hydrogen as demonstrated by Appell, et al. (4). Not only does carbon monoxide and water liquefy the coal to a greater extent, but carbon monoxide is much cheaper and easier to obtain than hydrogen. In the future, one possible source of carbon monoxide would be from a synthesis gas.

The purpose of this study was to determine the effects of two operating variables, temperature and pressure, on the liquefaction of a bituminous coal using batch autoclave reactors. Reaction temperatures were varied from 375°C to 475°C and initial carbon monoxide pressures were varied from 400 psi to 600 psi. Fixed operating variables were: solvent-to-coal ratio, water-to-coal ratio, reaction time, and solvent type. The following analyses were performed on the liquid product: percent benzene insolubles, total sulfur analysis, kinematic viscosity, carbon hydrogen analysis, specific gravity, reaction gas analysis, and heating value. In addition, an overall material balance and sulfur balance was performed.

CARBON MONOXIDE-STEAM LIQUEFACTION - LITERATURE SURVEY

The following is a summary of all currently published work on the CO-steam process.

Cellulose Liquefaction

The Bureau of Mines (1) has experimentally converted cellulose, primary constituent of organic solid waste, to a low sulfur oil. Many types of cellulosic wastes have been converted to oil by reaction with carbon monoxide and water at temperatures of 350°C to 400°C and pressures near 4000 psig in the presence of various catalysts and solvents. Cellulose conversions of 90 percent and better were obtained.

Sucrose liquefaction was also studied using a continuous reactor with maximum reaction conditions of 500°C and 5000 psig. Oil yields of over 30 percent were obtained. This compares with oil yields of 40 to 50 percent for the cellulose liquefaction.

Work was also done by Yavorsky, et al. (2) using the CO-steam process to liquefy urban refuse. A continuous reactor with a flow capacity of 1 lb per hour was used. Sucrose was used to select the optimum conditions for the reaction of refuse. Results from the sucrose runs indicated that conversion to oil was weakly dependent on total pressure and strongly temperature sensitive up to the optimum at 350°C. Oil yields of 23 percent for garbage up to 38 percent for sucrose were obtained. The ultimate theoretical yield of oil is 50 percent because approximately half the carbohydrate material is oxygen which cannot be converted to oil. A preliminary cost analysis showed that a large scale refuse conversion plant could be economically operated.

Early CO-Steam Work

In 1921 Fisher (3) reported using carbon monoxide and water in dehydrogenating coal. He reported higher yields of ether-soluble material using carbon monoxide and water than with hydrogen at similar conditions. Low overall conversion along with several other problems caused the carbon monoxide plus water approach to coal hydrogenation to be ignored after 1925.

Lignite Liquefaction

Batch tests were conducted by Appell, et al. (4,5,6,7) using a 500 ml rocking autoclave filled with 2 moles of carbon monoxide, lignite coal, water, and solvent. The objective of the work was to convert lignite to low sulfur fuel oil. It was believed that hydrogenation of coal using carbon monoxide and water proceeded via nascent hydrogen formed by the water-gas shift reaction. It now appears that carbon monoxide and water react with lignite in a more complex manner and that a number of factors are involved. Carbon monoxide and steam had higher conversion levels and reaction rates than those obtained using hydrogen under similar conditions. Results also indicated that both carbon monoxide and water must be present if good conversions are to be obtained, and that increasing the carbon monoxide pressure has a greater effect than increasing the steam pressure. These effects are dependent on the ratio of carbon monoxide to water. Conversion of lignite increases with increasing amounts of carbon monoxide and steam; however, there was an optimum temperature. Decreased conversion resulted after the temperatures were increased past 400°C.

Appell, et al. (8) also did work using different solvent types and catalysts. Several lignite tars and pitches were used as solvents and all gave good results for lignite liquefaction. The type of solvent was found more important than the amount. In the presence of a good solvent, it is possible to reduce the operating pressure and maintain acceptable conversions (85-90%). Heterocyclic amines were found to have a catalytic effect when used with carbon monoxide and water. The effectiveness of the heterocyclic amines was related to the increased boiling point of the solvent.

EXPERIMENTAL DESIGN

The object of this study was to determine the effects of varying reaction temperature and the initial moles of carbon monoxide (pressure) on the liquefaction of coal. The coal used in this study was a bituminous coal from the Pittsburgh number 8 seam, Ireland Mine, in West Virginia. A proximate analysis, ultimate analysis, and a sulfur form distribution can be seen in Table 1. The bituminous coal was selected because of the relative difficulty in liquefying it. Also, the primary thrust of previous work was in liquefying a low rank coal such as a lignite.

Reaction temperatures were examined at five levels from 375-475°C. These temperatures are somewhat higher than those used in previous CO-steam work; however, it was thought that more severe conditions were needed to convert the high rank bituminous coal. Five temperature levels were used in order to obtain a definite trend in conversion as a function of temperature.

Two major cost factors in liquefying coal are the capital costs for high pressure equipment and the carbon monoxide cost. Therefore, if comparatively low operating pressures yield an acceptable

Table 1. Ultimate and Proximate Analyses of Coal Used.

Coal: IM
Source: West Virginia
Rank: Bituminous

Proximate Analysis	As Received	Dry Basis
% Moisture	0.75	-
% Ash	12.99	13.16
% Volatile	34.68	39.94
% Fixed Carbon	51.58	51.90
	100.00	100.00
Ultimate Analysis		
% Moisture	0.75	-
% Carbon	61.09	61.55
% Hydrogen	4.54	4.57
% Nitrogen	0.95	0.96
% Chlorine	0.05	0.05
% Sulfur	4.14	4.18
% Ash	12.99	13.16
% Oxygen	15.49	15.53
	100.00	100.00
Heating Value (Btu)	11,143	11,227
% Total Sulfur	4.140	
% Organic Sulfur	3.157	
% Sulfate Sulfur	0.037	
% Pyritic Sulfur	0.946	

conversion of coal to oil, capital investment could be saved due to lower carbon monoxide consumption and utilization of lower pressure equipment. With this in mind, the low initial pressures of 400 to 600 psig of carbon monoxide were selected. Another factor in selecting the low initial pressures of carbon monoxide was the pressure limitations of the equipment used. The final pressures in some cases could exceed 3000 psig and the limit of the equipment is approximately 4000 psig at 400°C. It was decided not to exceed 600 psig initial pressure.

Fixed operating variables were as follows:
1) Reaction time: 1 hr
2) Water-to-coal weight ratio: 1.5:1
3) Solvent-to-coal weight ratio: 3:1
4) Solvent type: Creosote oil

Determination of the percent conversion of coal to liquid product was done with benzene in a Soxhlet extractor. The percent conversion was 100% less the percent of insoluble residue remaining after benzene extraction. Calculations were done on an ash-free basis. Sulfur analysis on the liquid product was done to determine the percent desulfurization of the coal and also in conjunction with the off-gas analysis allowed calculation of a sulfur balance. Carbon hydrogen analysis was done to determine the carbon-hydrogen ratio of the liquefied coal product to determine the approximate hydrogenation and chemical alteration of the coal through processing.

Table 2 shows the run numbers and the corresponding reaction conditions. Each variable combination was triply replicated, resulting in an A, B, and C run at each reaction condition. All experimental runs were performed in a random order, not in the order listed in Table 2.

Table 2. Run conditions.

Run No.	Reaction Temperature (°C)	Initial CO Pressure (psig) *
1	375	400
2	375	500
3	375	600
4	400	400
5	400	500
6	400	600
7	425	400
8	425	500
9	425	600
10	450	400
11	450	500
12	450	600
13	475	400
14	475	500
15	475	600

*At room temperature

EXPERIMENTAL PROCEDURE

The following procedures are listed in the order in which they were performed on each individual run (see Figure 1).

All experimental runs were performed in a random order.

Coal Preparation

1) Raw coal from the mine was crushed and screened and all that which passed through a 28 mesh screen was retained.

2) One large sample of -28 mesh coal was then split into 16 equal size samples using a Jones sample splitter. This procedure was done three times in order to make enough samples for all the runs to be carried out.

3) Each sample was placed in a beaker with a watch glass cover and used when needed.

Processing

Reaction of the coal proceeded as follows:

1) The empty reaction vessel and head assembly were weighed.

2) One hundred fifty grams of anthracene oil solvent, 75 grams of distilled water, and 50 grams of coal were weighed and added to the bomb.

3) The reaction vessel assembly was reassembled and then reweighed to determine the amount of reactants added.

4) The assembled reaction assembly was then inserted into the heating jacket and shaking assembly. The connecting lines were then attached and the thermocouple was inserted into the thermowell.

5) The reaction vessel was then purged three times by pressuring to 500 psig with helium, then venting to atmospheric pressure. On the third pressurization the reaction assembly and connecting lines were leak tested using a water-soap solution. If there were no leaks the reaction vessel was pressurized with carbon monoxide once to 500 psig, then to the initial carbon monoxide pressure required for that run. The system temperature was also recorded in order to determine the weight of CO added to the reaction vessel.

6) The heating jacket and shaker assembly were both turned on and the temperature controller for the heating jacket set at reaction temperature.

7) When the system reached reaction temperature the total pressure was taken. (Three runs were done at the same conditions, only on the third run the pressure was not checked so no gas is lost. This was done so that an accurate overall material balance could be obtained.)

8) The system was allowed to react for one hour at which time both the shaker and the heater were switched off, the connecting line to the vessel was removed and the reaction vessel assembly was removed from the heating jacket. The reaction vessel was then placed in front of a fan and cooled to room temperature. This caused the temperature inside the bomb to decrease rapidly, thus quenching the reaction.

9) When the reaction vessel had cooled to room temperature the reaction vessel assembly was then weighed and carried to the gas analysis system.

10) After completion of the gas analysis, the reaction vessel was opened and the liquid product poured out into a beaker. In order to remove all the liquid product the inside of the reaction vessel was washed with acetone. The acetone wash was then poured in with the liquid product. This mixture was then placed in an oven at approximately 50°C until all the acetone was vaporized. The beaker was then weighed to determine the amount of liquid product recovered.

EQUIPMENT

Two reactor systems of the batch autoclave generic type were used in this study. A gas delivery system, a reaction vessel, and a shaking assembly were the functional parts of the reactor systems. The reaction vessels were manufactured by the American Instrument Company (AMINCO) of Silver Spring, Maryland, and were from the 4 3/8-in. series. Both reaction vessels had inside depths of 10 in., inside diam. of 3 5/16 in., and approximate weights of 50 lbs. The vessels were fabricated from AISI 347 stainless steel. The vessels had a working pressure rating of 5,050 psi at 100°F and had an effective volume of 1410 ml. Two shaking assemblies were used in the reactor system. The shaking assemblies were standard Aminco 4 3/8-in. series and consisted of a 3,000-watt, 208-volt heating jacket mounted on a rocker assembly. The rockers for the shaking assemblies were actuated by 1/3-hp, 110-volt motors driving eccentric levers connected to the heating jackets. The heating jacket had the capacity to heat from room temperature to 400°C in approximately 1 1/2 hr. Aminco 30,000 psi valves and fittings were used to regulate the inlet and exit of the reaction gases from each reaction vessel. One reactor system was equipped with 0 to 3,000 pressure gauge. The other had a 0-5,000 psi pressure gauge. Tubing used on the shaking assemblies was 304 stainless steel, 1/4-in. o.d., and rated for operation at 100,000 psi at 100°F.

Leeds and Northrup Electromax III controllers, with Model 11906 SCR final control elements were used for temperature control. Temperatures were recorded on a Honeywell Electronik III two-channel continuous recorder. The temperature sensors were chromel-alumel thermocouples.

Both shaking assemblies were connected to purging-charging gas delivery systems. Each of these systems consisted of a helium cylinder, a carbon-monoxide gas cylinder, pressure regulators for each cylinder, and Aminco stainless steel tubing and fittings similar to those used on the shaking assemblies.

To analyze for the total sulfur content of the liquid coal, the Leco induction furnace technique was used. A gas purification train, an induction furnace and a semi-automatic titrator unit were the three components of the analysis system. The gas purifying train contained an acid tower, a dry reagent tower, and a rotameter, and was used to measure and scrub any residual sulfur from the entering oxygen. The induction furnace was a Leco model 521, equipped with the "L" modification on the combustion chamber. A special feature of the "L" modification was the inclusion of a high temperature igniter in the combustion chamber. The exhaust gases from the induction furnace combustion chamber were sent through an electrically heated glass delivery tube and into the Leco semi-automatic titrator model 518. The semi-automatic titrator used an idiometric reaction with a color change endpoint to analyze the combustion gases. The reported accuracy of the test is ±0.01 weight percent sulfur. The Leco induction furnace technique used was ASTM D1552-64 (American Society for Testing and Materials, 1968, pp. 377-383).

Analysis of the reaction product gas was accomplished by gas chromatography. The gas chromatograph was fitted with an external valve oven, two eight-foot Porapak Q columns, and one six-foot molecular sieve column in a series by-pass arrangement. The columns were heated to 170°C. The chromatograph was supplied with a helium carrier gas. A heated thermal conductivity detector was used. The following components could be quantitatively determined:

1) CO
2) CO_2
3) CH_4
4) C_2H_6
5) C_3H_8
6) $i\text{-}C_4H_{10}$
7) $n\text{-}C_4H_{10}$
8) H_2S
9) COS

The hydrogen composition was determined indirectly using the average molecular weight and the hydrogen free gas composition of the reaction gases. The accuracy of the reported gas weight percents are ±2.5 percent. Calibration of the gas chromatograph was accomplished by determining an average response factor for pure components relative to nitrogen, and an average retention time for each component was established.

RESULTS

Percent Conversion of Coal to Liquid

The results of the Soxhlet extractions are summarized in Figure 2. One definite trend shown by the data is that higher temperatures favor the liquefaction of coal. The carbon monoxide pressure effects are not as obvious. However, a trend can be seen if the highest and lowest pressure level are compared. At all but the lowest temperature investigated (375°C) the 600 psi conversion isobar was above the 400 psi conversion isobar. This suggests that higher initial pressures of carbon monoxide enhance the liquefaction of coal, which agrees with results from the Bureau of Mines research (5). Appell and Wender found that an increase of initial carbon monoxide pressure from 500 psi to 1100 psi results in an increase in conversion from approximately 40% to 70%, for a bituminous coal. Reaction temperatures and reaction times for the Bureau of Mines study were 425°C and 2 hours, respectively. A different solvent type, solvent-to-coal ratio, and water-to-coal ratio were used so the Bureau of Mines results cannot be directly compared with the results reported here. However, the conversions found in this study were higher than conversions of a bituminous coal reported by the Bureau of Mines. When all three isobars are plotted (Figure 2) no pressure trend seems apparent. The 500 psi isobar crosses both the 400 psi and the 600 psi isobars. This suggests that the pressure levels chosen were too close together for any trend to be observed.

Figure 3 shows the effect of hydrogen partial pressure on the conversion of the coal. The data was scattered, however the trend shows that increasing the hydrogen partial pressure increases the coal conversion. The reaction gas analysis was used to determine hydrogen partial pressures.

One problem in the analysis of the liquefied coal was the inaccuracy in the Soxhlet extraction procedure. Repeatability tests were done and the error in the Soxhlet extractions ranged between 2 to 15 percent.

The temperature and pressure readings reported have an accuracy of ±2.5°C and ±10 psi respectively.

Sulfur Balances

A tabular comparison of the sulfur balances for all the C runs is shown in Table 3.

Table 3. Sulfur Balance (all weights in grams).

Run No.	Sulfur In Total	Sulfur Out (Reaction Gas)	Sulfur Out (Liq. Coal)	Sulfur Out Total	Difference	% Error
1C	2.7	1.0	2.0	3.0	+0.3	11.1
2C	2.8	1.3	1.9	3.2	+0.4	14.2
3C	2.7	1.0	2.0	3.0	+0.3	11.1
4C	2.7	1.4	1.8	3.2	+0.5	18.5
5C	2.7	0.4	1.9	2.3	-0.4	14.8
6C	2.8	1.3	1.7	3.0	+0.2	7.1
7C	2.7	2.2	1.7	3.9	+1.2	44.4
8C	2.7	1.6	1.5	3.1	+0.4	14.8
9C	2.7	1.3	1.7	3.0	+0.3	11.1
10C	2.7	1.5	1.5	3.0	+0.3	11.1
11C	2.7	2.0	1.4	3.4	+0.7	10.3
12C	2.7	1.6	1.5	3.1	+0.4	14.8
13C	2.7	1.7	1.0	2.7	0.0	0.0
14C	2.7	1.6	1.1	2.7	0.0	0.0
15C	2.7	1.6	1.1	2.7	0.0	0.0

The largest source for error in the sulfur balance calculations was the determination of the percent sulfur in the reaction gas. The determination of the sulfur content in the reaction gas was done using a gas chromatograph. The sulfur percentages can have errors up to 4.5 percent.

The error in the sulfur balances range from 0.0 to 44 percent. The average error was approximately 10 to 15 percent with more apparent sulfur being accounted for in the products than in the combined feed. This suggests that the sulfur analysis on the raw coal or the creosote oil was low or the percent sulfur in either the reaction gas or liquid coal was consistently high. Despite the aforementioned problems the results from both the sulfur balance and the overall material balance are encouraging.

Sulfur Removal

Total sulfur analyses on the liquid coal and solvent mixture are shown in Figure 4. The points plotted in Figure 4 were found from the average of the three runs at the same temperature and pressure. Increases in reaction temperature and carbon monoxide pressure decrease the amount of sulfur in the liquid product. The only deviation from this general trend occurs at 375°C and 400°C at an initial carbon monoxide pressure of 400 psi. At both these temperatures the lowest carbon monoxide pressure had better desulfurization than the higher pressures.

Following is a possible explanation of the crossing of the desulfurization isobars in Figure 4. Several considerations are listed below:

1) Higher reaction pressures were obtained by charging more carbon monoxide to the reactor. Since the amount of water charged is fixed, a higher carbon monoxide-to-water ratio increases the yield of hydrogen produced from the shift reaction.

2) Higher temperature increases the reaction rates for both the hydrogen desulfurization reaction and the shift conversion reaction.

3) However, the thermodynamic yields of H_2S and H_2 from the desulfurization reaction and the shift conversion reaction are greater at lower temperatures.

4) Partial desulfurization of coal occurs by devolatilization of the coal. More devolatilization occurs at lower system pressures.

Items 1 and 2 indicate that greater desulfurization occurs at higher temperature and pressure. However, item 3 indicates low temperatures are more favorable to desulfurization, and item 4 indicates an advantage for low pressures. These considerations offer a partial explanation for the reversal of pressure effects at lower temperatures and the flat temperature response at the lower temperatures investigated.

Figure 5 shows that the best desulfurization occurs at higher hydrogen partial pressures. This coincides with the higher temperatures investigated, and suggests that the shift reaction was going more to completion at higher temperatures as indicated in item 2.

The temperature effects on desulfurization are much more apparent. An increase in reaction temperature of 100°C approximately doubles the desulfurization of the coal.

The error in the Leco procedure for determining the total sulfur in the coal product is ±0.01 percent, which is not significant in comparison with the total sulfur percentages in the oil of 0.6 to 1.0 percent.

Actual desulfurization of the coal ranged from 23 to 57 percent. Desulfurization results on the same coal using hydrogen at similar reaction conditions were reported to be 77 percent desulfurization at 400°C (9). Approximately 25 percent of the sulfur was removed using the CO-steam process at the same reaction temperatures. Apparently pure hydrogen gives much better desulfurization than carbon monoxide and water. Better desulfurization with hydrogen should be expected since there is more hydrogen in the gas phase present to react with the sulfur.

The primary desulfurization reaction that is favored by chemical equilibrium is reaction of sulfide sulfur in the coal with hydrogen gas. The reaction is:

$$RSR(\ell) + 2H_2(g) \rightarrow 2RH(g) + H_2S(g)$$

A plot of coal desulfurization versus hydrogen partial pressure and reaction temperature was made to determine the effects of each on desulfurization. The plots are shown in Figures 5 and 6. Two conclusions can be made from these plots. One, desulfurization increases with an increase in hydrogen partial pressure, and desulfurization increases with an increase in reaction temperature. The hydrogen partial pressure has to be increased by 3 times to double the desulfurization, however, and increase of 25 percent in the reaction temperature doubles the desulfurization. It therefore appears that reaction temperature has a stronger effect on desulfurization than does hydrogen partial pressure.

It must be noted that the experimental runs were done in batch reactors. As a result the desulfurization is limited by equilibrium and therefore, the desulfurization obtained may not be the maximum attainable under the reaction conditions studied.

Carbon-Hydrogen Ratio of Coal Liquid

Tabular values of the C/H weight ratio are shown in Table 4. There appears to be no discernible trend in these results. The C/H ratios ranged from 14.5 to 15.8 with a standard deviation of 0.32.

The carbon hydrogen ratio of the raw coal and the raw solvent is 13.45 and 15.31 respectively. The carbon hydrogen ratio of the raw coal plus solvent slurry is 14.85. The average carbon hydrogen ratio of the mixture after treating was 14.97. Therefore, it appears that little hydrogenation of the coal and solvent occurred.

Table 4. Carbon-Hydrogen Ratios of Liquid Coal Product.

Run No.	C/H	Run No.	C/H
1	14.7	9	14.6
1	14.8	9	15.0
1	14.6	9	14.7
2	14.9	10	15.2
2	14.8	10	15.5
2	14.8	10	15.0
3	15.0	11	15.0
3	14.5	11	15.5
3	14.9	11	15.0
4	14.9	12	14.5
4	14.7	12	14.7
4	15.3	12	14.7
5	14.9	13	15.8
5	14.7	13	15.4
5	14.9	13	15.6
6	14.7	14	15.6
6	14.6	14	15.3
6	14.8	14	15.3
7	15.1	15	15.4
7	15.1	15	15.3
7	14.9	15	15.3
8	14.9		
8	14.8		
8	14.8		

Final Reaction Pressures

Reaction pressures were not taken on the C runs so that an accurate material balance could be calculated. A plot of reaction pressures is shown in Fig. 7.

Reaction pressures increased with increased reaction temperature and with increased initial carbon monoxide pressure. The increase was not linear but slightly exponential. The highest reaction pressure encountered was 3540 psig at 475°C and an initial carbon monoxide pressure of 600 psig.

Viscosity of the Liquid Coal

Viscosities ranged from 39 SSU to 77 SSU. Liquid viscosities are shown in Table 5. Product viscosity decreased with an increase in both temperature and pressure with reaction temperature having a greater effect on the product viscosity than reaction pressure. At the lowest reaction temperature the pressure effect was reversed. The higher reaction pressures and temperatures cracked the coal molecules to a greater extent making the liquid product less viscous.

It must be noted that the viscosities were taken of the mixture of both treated coal and solvent with the unreacted coal being separated before analysis. Several samples were analyzed twice to check the results. A maximum variation of 2 Saybolt seconds, or approximately 3 percent error, was found.

Table 5. Kinematic Viscosity of Liquid Coal at 210°F.

	SSU (sec)		Kinematic Viscosity (cst.)	
Run No.	1	2	1	2
1	68	67	12.7	
2	71		13.4	
3	74	76	14.2	14.7
4	77		14.9	
5	72	73	13.7	13.9
6	61		10.9	
7	63	62	11.4	11.2
8	60		10.6	
9	50		7.9	
10	55	55	9.3	9.3
11	47		7.1	
12	44	44	6.2	6.2
13	45		6.5	
14	45		6.5	
15	39	40	4.7	5.0

Heating Values of Liquid Coal

Heating values were determined on the mixture of liquid coal and solvent after treating. The heating values are shown in Table 6. The untreated mixture of coal and solvent had a heating value of 15,388 BTU/lb. After treating the heating values of the mixture ranged from 16,873 BTU/lb to 17,818 BTU/lb. Therefore, the heating values were increased approximately 10 percent through treating.

Table 6. Liquid Coal and Solvent Mixture Heating Values.

Run No.	Heating Values BTU/lb
1A	16,922
2A	17,045
3A	16,889
4A	16,902
5A	17,157
6A	17,090
7A	17,178
8A	17,320
9A	16,873
10A	17,818
11A	16,994
12A	17,269
13A	17,278
14A	17,294
15A	17,407
Creosote Oil	16,775
Coal (Dry)	11,227

CONCLUSIONS

The following conclusions can be made from this study.

1) Conversion of coal to liquid increases with an increase in reaction temperature over the range of 375°C to 475°C. However, the total system pressure, over the range of 2300 psig to 3500 psig, does not appear to have any definite effect on coal conversion.

2) Conversion of bituminous coal to liquid was better than conversions reported in previous studies at the same reaction conditions.

3) Desulfurization increases with an increase in reaction temperature over the range of 375°C to 475°C. Again, the pressure effects on coal desulfurization were not apparent from this study.

4) Desulfurization results found in this study using the CO-steam process were not as good as the desulfurization potentially attainable using pure hydrogen.

5) Desulfurization increases with an increase in hydrogen partial pressure from 100 psia to 800 psia.

6) Maximum desulfurization attained with the CO-steam process in the temperature and pressure range studied was 57 percent.

7) Reaction pressures increase exponentially with increases in reaction temperature over the range studied.

8) The carbon-hydrogen ratio of the coal and solvent mixture did not change appreciably through processing in the temperature and pressure ranges studied.

9) Liquid coal and solvent viscosities decrease with increases in both reaction temperature and reaction pressures over the range studied.

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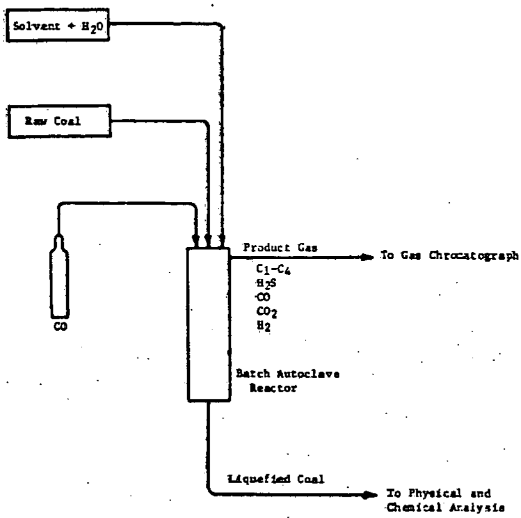

Figure 1. Simplified Process Flow Diagram, CO-Steam Liquefaction of Coal.

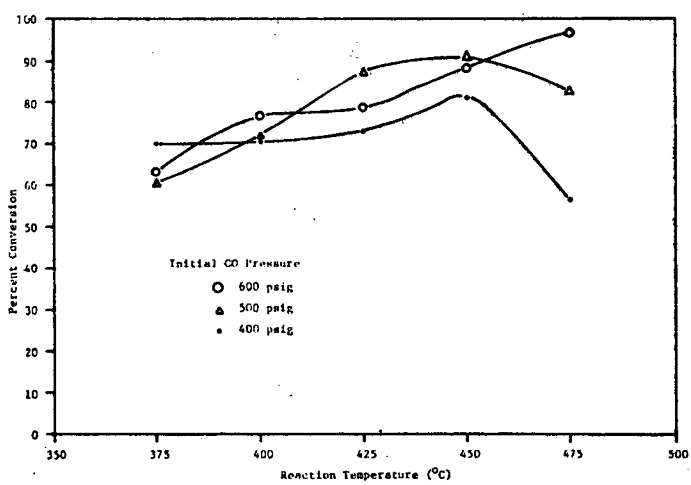

Figure 2. Weight Percent Conversion of Solid Coal to Liquid Coal.

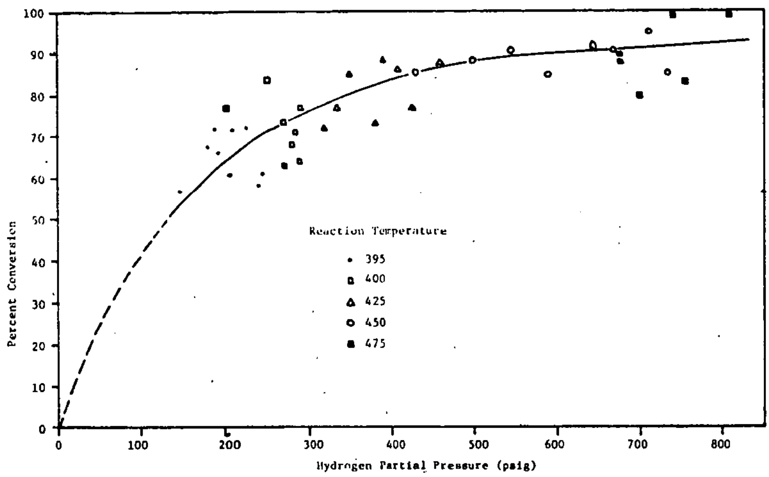

Figure 3. Coal Conversion as a Function of Hydrogen Partial Pressure.

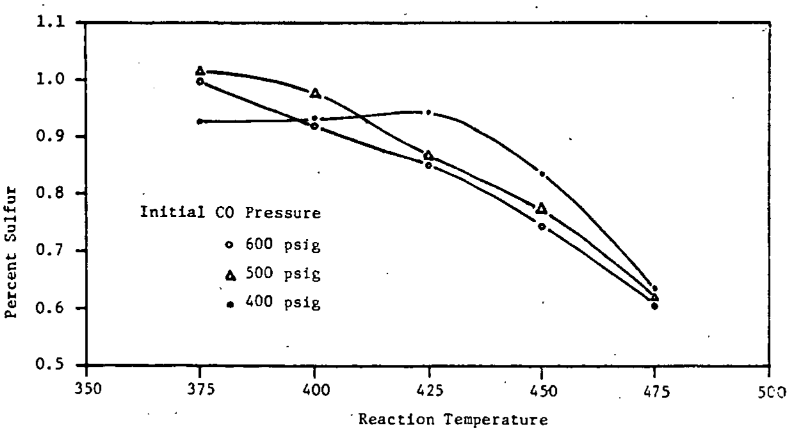

Figure 4. Weight Percent Sulfur in Liquid Coal Product.

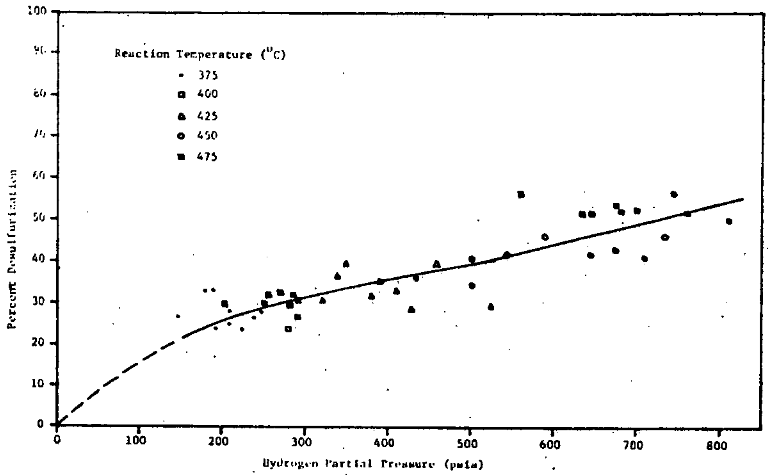

Figure 5. Coal Desulfurization as a Function of Hydrogen Partial Pressure.

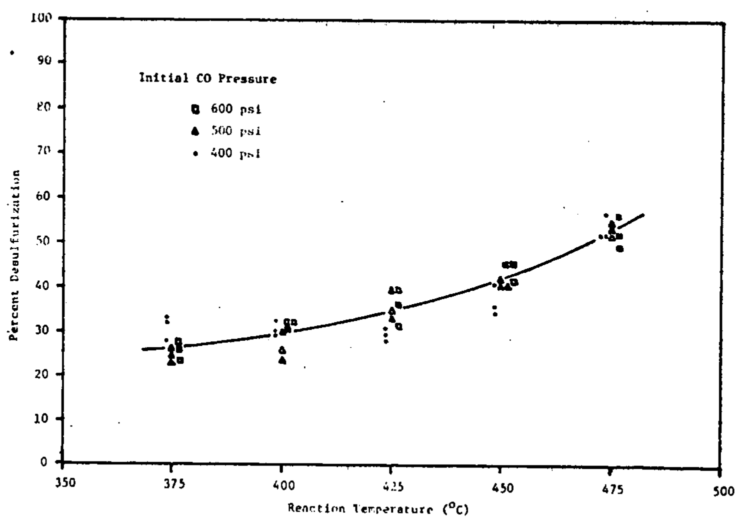

Figure 6. Coal Desulfurization as a Function of Reaction Temperature.

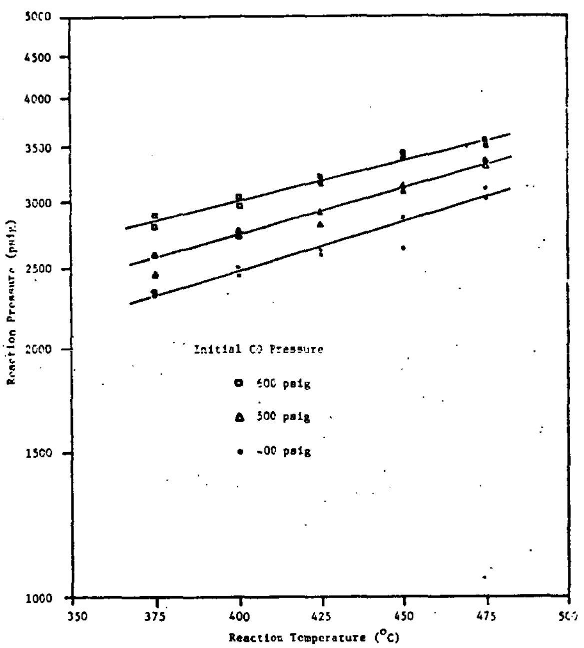

Figure 7. Final Reaction Pressures.

CATALYTIC COAL LIQUEFACTION USING SYNTHESIS GAS

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INTRODUCTION

Recent energy shortages and environmental problems underline the great importance of desulfurizing coal to produce low-sulfur fuels. Efforts are in progress in many organizations to develop catalytic hydrogenation processes for producing liquid fuel from coal. Unfortunately, most hydrogenation processes require enormous amounts of expensive hydrogen and some significant breakthrough is needed before an economical process can be realized. A major effort must be made to reduce the high cost of hydrogen. One approach is to utilize low cost synthesis gas as the process gas to achieve equal or better results.

There have been some attempts to use carbon monoxide or carbon monoxide-containing gas for liquefying lignite (1), hydrotreating hydrocarbonaceous liquids (2), and desulfurizing heavy liquid hydrocarbon (3). The process of liquefying lignite with carbon monoxide and water does not work well on bituminous coals, and does not desulfurize coal very effectively. The hydrotreating and desulfurization of heavy liquid hydrocarbons appears to proceed well with carbon monoxide or carbon monoxide-containing gas in the presence of steam and an active metal catalyst. We have also reported that organic wastes have been hydrotreated with synthesis gas and cobalt molybdate-sodium carbonate catalyst and converted to oil (4).

The present work deals with an effort to develop an economical process for coal liquefaction-hydrodesulfurization using low cost synthesis gas in the presence of cobalt molybdate and sodium carbonate catalysts. While hydrogenation and desulfurization are catalyzed by cobalt molybdate, the water-gas shift reaction and reduction of coal by carbon monoxide are catalyzed by sodium carbonate. Hydrogen consumed is replenished partly during the hydrogenation by the following catalytic reaction, $CO + H_2O \rightarrow H_2 + CO_2$. As a result, an effective hydrogenation is accomplished by eliminating large amounts of the oxygen in coal as carbon dioxide. It is noteworthy that the conversion of the oxygen in coal to water is one of the main hydrogen-consuming reactions in coal liquefaction.

EXPERIMENTAL

The liquefaction of coal was studied in a 500-ml magnetically-stirred stainless steel autoclave. Illinois No. 6 high-volatile bituminous coal and Kentucky Homestead high-volatile bituminous coal were used (table 1). A high boiling alkylnaphthalene-based oil (boiling above 235°C) and oil products from the Kentucky bituminous coal -- SYNTHOIL (5) -- were used as vehicles. The catalyst was a silica promoted cobalt molybdate supported on alumina (Harshaw CoMo 0402T)* used either with or without sodium carbonate. The catalyst pellets were crushed before use. For most of these experiments, hydrogen and synthesis gas with H_2:CO ratios of 1:1 and 2:1 were used at initial pressures of 1500 to 1800 psi. Operating pressures ranged from 2400 to 3400 psi at reaction temperatures of 370° to 450°C and the

*Reference to a product name is made to facilitate understanding and does not imply endorsement by the U. S. Bureau of Mines.

reaction was maintained for 5 to 60 minutes at the reaction temperature. After the experiment, rapid internal water cooling of the autoclave to ambient temperature was achieved. Total products were filtered at ambient or warmer temperatures to obtain liquid oils. Filter cakes containing residue and water were extracted by benzene. The water was removed by azeotropic distillation, and the remaining oil was recovered by removing the benzene with a rotary vacuum evaporator. Gaseous products were analyzed by mass spectrometry. Data on conversion, oil yield, hydrogen consumption, and carbon dioxide formation, etc., are given as weight-percent based on moisture- and ash-free (maf) coal.

TABLE 1. Analyses of coal, percent

Coal	C	H	N	S	O	Ash	Moisture	VM
Illinois No. 6 bituminous								
As used	64.8	5.2	1.3	3.46	14.0	11.2	6.0	38.3
maf	78.3	5.5	1.6	4.18	10.5			46.3
Kentucky Homestead bituminous								
As used	58.8	4.9	1.2	5.16	14.4	15.5	7.1	35.7
maf	75.9	5.4	1.6	6.67	10.5			46.1

RESULTS AND DISCUSSION

Using $1H_2$:1CO Synthesis Gas. In initial experiments, high sulfur bituminous coal was liquefied and desulfurized by hydrotreating with synthesis gas (approximately equal parts of hydrogen and carbon monoxide) in the presence of CoMo-Na_2CO_3 catalyst and an alkylnaphthalene vehicle oil (S = 0.42%). Using Illinois No. 6 hvbb coal (S = 4.18 maf %) with 25 to 35% added moisture at a coal:vehicle ratio of 1:2.3, 3400 to 4000 psi operating pressures, and 450°C reaction temperature, averages of 91% conversion and 58% oil yield were obtained. The oil product contained an average of 0.38% sulfur.

Further experiments were carried out using a benzene soluble oil product (S = 0.5%, kinematic viscosity = 2515 centistokes at 60°C) from Kentucky bituminous coal as the starting vehicle at an initial pressure of 1500 psi and 430°C reaction temperature. Various amounts of water (0 to 15 parts per 100 parts of coal plus vehicle) were added in different runs to determine the effect of moisture content of coal. In each succeeding run, the oil product recovered from the preceding run was used as vehicle. The results are shown in Table 2 and compared with that obtained from hydrogen runs which also used the same coal oil as the starting vehicle. Average data of three successive hydrogen runs are given in the table. The degree of hydrodesulfurization appears to be satisfactory at 430°C for both synthesis gas and hydrogen runs, but there is a significant decrease in hydrogen consumption and an increase in carbon dioxide formation in the synthesis gas runs. In the synthesis gas runs, the addition of water improved desulfurization and caused less hydrogen but more carbon monoxide to be consumed. The increase of moisture content has no significant effect, however, on coal conversion nor oil yield.

TABLE 2. Effect of water on hydrotreating of coal
Illinois bituminous coal:recycle oil = 1:2.3
(1,500 psi initial pressure, 430°C, 30 min)

	Synthesis gas ($1H_2$:1CO)				H_2
Catalyst	CoMo[1] + Na_2CO_3[1]				CoMo[1]
Water added, parts/100 parts coal + vehicle	0	5	10	15	0
Operating pressure, psi	2,500	3,000	3,400	3,800	2,400
Conversion, %	88	92	92	94	91
Oil yield, %	55	62	58	57	62
H_2 consumption, %	4.6	3.0	1.5	1.2	6.0
CO consumption, %	50	65	90	94	-
CO_2 formation, %	46	85	108	113	1
CH_4 formation, %	5.4	4.5	4.9	5.0	3.0
S in oil product, %	.41	.37	.29	.29	.21
Kinematic viscosity of oil product, cs at 60°C	109	88	57	36	57

[1] Two parts per hundred parts coal plus vehicle.

Data are given in weight percent of maf coal.

Comparisons between the use of synthesis gas and hydrogen were also made at various temperatures. Data shown in Table 3 are taken from the last of three successive runs at each temperature. With decreasing temperature, using either gas,conversion decreases, oil yield increases, sulfur content in oil increases, and kinematic viscosity of oil product increases. In the hydrogen runs, hydrogen consumption is far greater and oil viscosity is more susceptible to temperature change. It is noteworthy that the product from reaction with synthesis gas and CoMo-Na_2CO_3 catalyst at 400°C is quite fluid at room temperature even after many recycle runs. On the other hand, the product from reaction with hydrogen and CoMo catalyst at the same temperature is quite viscous and the viscosity increases with each recycle run. The possibility of obtaining fluid and easily filtered oil products at lower temperatures in the synthesis gas-CoMo-Na_2CO_3 system than in the hydrogen-CoMo system may prove to be advantageous. The amount of low molecular weight hydrocarbon gases produced was small but increased with temperature.

Additional comparative data were obtained using Kentucky bituminous coal. The starting vehicle was pretreated with synthesis gas or hydrogen at specific conditions (see Table 4) prior to its use for subsequent coal liquefaction experiments. Again, at 400°C, the product from the reaction with synthesis gas, steam, and CoMo-Na_2CO_3 catalyst was least viscous.

Using $2H_2$:1CO Synthesis Gas. The effect of reaction time was studied using $2H_2$:1CO synthesis gas. Experiments were conducted at an operating pressure of about 3,000 psi and reaction temperatures of 425° to 450°C. Kentucky bituminous coal and a SYNTHOIL product (S = 0.17%, kinematic viscosity = 18 cs at 60°C) were used at a coal:vehicle ratio of 1:2.3. In the synthesis gas runs, 5 parts of water, 2 parts of CoMo catalyst, and 1 part of Na_2CO_3 catalyst per hundred parts of coal plus vehicle were added. Coal conversions of 85 to 92% and oil yields of 40 to 60% were obtained with 5 to 60 minutes reaction times in both synthesis gas and hydrogen runs (see Figure 1). No significant difference was found between the two systems. The oil yield was nearly constant for all reaction times at 425°C, but decreased significantly after 15 minutes reaction time at 450°C. At high temperatures, long residence time causes further cracking of the product oil to form low molecular weight hydrocarbons. These observations suggest that the optimum liquefaction temperature is in the vicinity of 425° to 450°C and that a short residence time is practical.

TABLE 3. Hydrotreating of coal at various temperatures
(Illinois bituminous coal:recycle oil = 1:2.3, 1500 psi initial pressure, 30 min.)

	Synthesis gas (1:1)			H_2	
Catalyst	CoMo[1] + Na_2CO_3[1]			CoMo[1]	
Water added, parts/100 parts coal + vehicle	10			0	
Temperature, °C	430	400	370	430	400
Operating pressure, psi	3,400	3,400	3,400	2,400	2,400
Conversion, %	95	92	87	91	86
Oil yield, %	58	61	65	62	63
H_2 consumption, %	1.5	0.2	-0.5	6	4
CO consumption, %	90	85	85	-	-
CO_2 formation, %	108	101	103	1	1
CH_4 formation, %	4.9	3.0	2.1	3.0	1.2
Oil analysis, %					
C	87.7	86.7		89.0	87.4
H	7.6	8.0		7.7	8.1
N	1.4	1.5		1.1	1.2
S	0.29	0.36	0.39	0.21	0.34
O	3.0	3.4		2.0	3.0
Kinematic viscosity, cs at 60°C	57	148	1,480	57	2,967

[1] Two parts per hundred parts coal + vehicle.

Data are given in weight percent of maf coal.

Figure 2 shows that the sulfur content and the viscosity of the oil product both decrease with increasing temperature and reaction time, but at the expense of the oil yield at 450°C. Regardless of the reaction temperature, the oil properties correlated well with the net amount of H_2 consumed in the respective system. As shown in Figure 3, the viscosity and the sulfur content of the oil product decrease with the amount of H_2 consumed. It is evident that the amount of H_2 required to attain the same level of oil quality is considerably less in the synthesis gas system than in the hydrogen system (see solid lines). When the amount of H_2 formed (equal to the amount of CO_2 formed) by the water-gas shift reaction is taken into account (dashed lines in Figure 3), the consumption of hydrogen is still less with synthesis gas. This finding suggests that carbon monoxide could be beneficial to the coal liquefaction reaction. Carbon monoxide could act to depolymerize coal, to stabilize the decomposition radicals, to prevent repolymerization, and to deoxygenate coal.

The Consumption of Reactant Gases. The consumption of gases in the coal liquefaction reaction varies with reaction variables. In particular, the consumption of synthesis gas depends a great deal on the H_2/CO ratio, the amount of water, and the presence or absence of Na_2CO_3 catalyst because of the concurrent water-gas shift reaction taking place. Table 5 shows some analyses of off-gas obtained at various conditions. The operating pressure was 3,000 psi and the amount of water added was 5 parts per hundred parts coal plus vehicle in each of the synthesis gas runs. The gas consumptions are also shown.

TABLE 4. Hydrotreating of Kentucky bituminous coal at 400°C
(1,500 psi initial pressure, 30 minutes)

	Synthesis gas (1:1)		H_2
Catalyst	CoMo[1]	CoMo[1] + Na_2CO_3[1]	CoMo[1]
H_2O added, parts/100 parts coal and vehicle	0	10	0
Operating pressure, psi	2,400	3,100	2,500
Hydrotreating vehicle			
S in oil product, %	0.31	0.30	0.29
Kinematic viscosity at 60°C	411	171	1,079
Hydrotreating coal (coal:vehicle = 1:2.3)			
S in oil product, %	0.30	0.30	0.33
Kinematic viscosity, cs at 60°C	348	231	2,330
Conversion, %	83	88	85
Oil yield, %	55	60	63
H_2 consumption, %	3.7	1.0	4.0
CO consumption, %	41	80	-
CO_2 formation, %	27	91	0.6
CH_4 formation, %	3.0	2.8	1.2

[1] Two parts of pulverized material per 100 parts coal and vehicle.

Data are given in weight percent of maf coal.

The significant formation of carbon dioxide indicates that, in the catalytic hydrotreating of coal using synthesis gas, large amounts of the oxygen in coal are removed as carbon dioxide. The H_2/CO ratio of the off-gas leaving the reactor is greater than the feed gas. The total gas consumption and the CO/H_2 consumption ratio (scf of CO consumed divided by scf of H_2 consumed) are greater with $1H_2$:1CO synthesis gas than with $2H_2$:1CO synthesis gas. The H_2 consumption is greatest when hydrogen is used.

Liquefaction Process Using Synthesis Gas. It appears that synthesis gas with CoMo-Na_2CO_3 catalyst can be used in a coal liquefaction process. Sodium carbonate can be dissolved in the added water and mixed with coal. As an illustration, a simplified schematic flow diagram of a conceptual coal liquefaction process using synthesis gas is shown in Figure 4. The gas stream flow in scfh (on 100 lb/hr coal feed basis) and volume percent are shown in Table 6. The calculation was based on the data at 450°C and 15 minutes (see Table 5) requiring a CO/H_2 consumption ratio of 1.33. Thus a supply of 0.75 H_2:1CO synthesis gas is introduced to the recycle gas ($H_2/CO = 2.9$) to make up the feed gas with the composition of $2H_2$:1CO. Using an oil yield of 3 barrels per ton of coal, the synthesis gas (0.75 H_2:1CO) consumption is calculated to be 4,000 scf per barrel of oil. In comparison, based on the similar data for the hydrogen run at 450°C and 15 minutes (Table 5), the hydrogen consumption would be 4,700 scf per barrel of oil when the feed gas is hydrogen.

TABLE 5. Analyses of off-gases and gas balance

(Coal:vehicle = 1:2.3, operating pressure = 3,000 psi)

Feed gas	Synthesis gas (H_2:CO = 1:1)		Synthesis gas (H_2:CO = 2:1)		H_2	
Temperature, °C	430	450	425	450	425	450
Time, min.	30	30	30	15	30	15
Water added, parts/100 parts coal + vehicle	5	5	5	5		
Catalyst	CoMo[1] + Na_2CO_3[1]		CoMo[1] + Na_2CO_3[a]		CoMo[1]	
Off-gas analysis, %						
H_2	39.8	41.8	62.7	64.5	96.1	96.0
CH_4	3.5	4.2	1.8	2.5	1.2	1.7
C_2H_6	1.4	1.0	0.7	1.0	0.6	0.7
CO	29.3	31.5	23.4	22.5		
CO_2	24.4	20.5	10.1	9.5	0.2	0.1
H_2/CO ratio	1.35	1.33	2.68	2.86		
Gas balance, scf/lb maf coal						
Input	33	33	34	34	40	40
Output	27.8	27.0	31.2	30.3	32.5	32.2
H_2 consumed	5.5	6.3	3.1	3.3	8.8	9.0
CO consumed	8.7	10.3	4.2	4.4		
CO_2 formed	7.2	8.2	3.2	2.8		
CO/H_2 consumption ratio	1.58	1.64	1.35	1.33		

[1] Two parts per hundred parts coal plus vehicle.
[a] One part per hundred parts coal plus vehicle.

TABLE 6. Gas stream flows

(Basis: 100 lb/hr coal feed)

Stream	Total flow, scfh	Gas composition, %				
		H_2	CH_4	C_2H_6	CO	CO_2
1	2,700	67			33	
2	2,400	64.5	2.5	1.0	22.5	9.5
3	2,090	74			26	
4	610	43			57	

The use of synthesis gas as the feed gas may be applied to SYNTHOIL, H-Coal, CONSOL, and other catalytic hydrogenation processes. The advantages are obvious: (1) the high cost of hydrogen production is saved, and the thermal efficiency increased; (2) the synthesis gas usage is lower, and the supply can be obtained at less cost than hydrogen from the gasification of the char produced in the process; and (3) the off-gas, after scrubbing out carbon dioxide and hydrogen sulfide, is a low-Btu gas. With the H_2/CO ratio of about 3, it is suitable for use in methane production or methanol synthesis. If one recycles the gas only a small bleed stream is necessary to keep CH_4 level down. The bleed gas could be burned for process heat.

CONCLUSIONS

High sulfur bituminous coal can be liquefied and desulfurized by hydrotreating with synthesis gas at 3,000 psi and 425° to 450°C in the presence of cobalt molybdate-sodium carbonate catalyst, steam, and recycle oil. The sulfur content and the viscosity of the oil product both decrease with the amount of hydrogen consumed whether synthesis gas or hydrogen is used as the reactant gas, but less total hydrogen is required for the same oil product quality when synthesis gas is used. The synthesis gas consumption is low -- 4,000 scf per barrel of liquid fuel product. The cost of hydrogen production is saved, and the off-gas can be optionally burned as a low-Btu gas or utilized for methane production or methanol synthesis.

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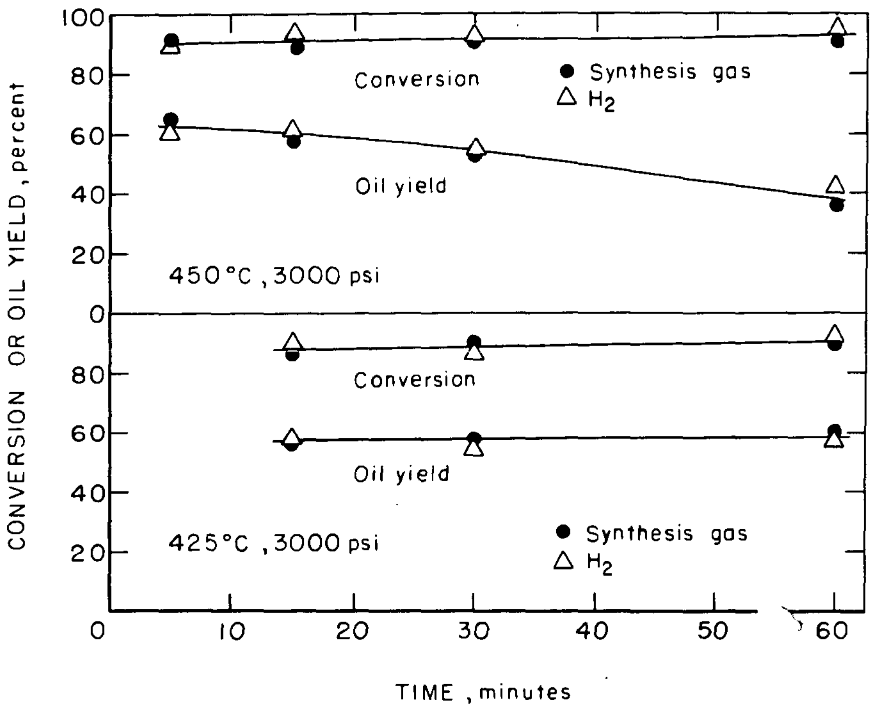

Figure 1 - Conversion and oil yield vs reaction time.

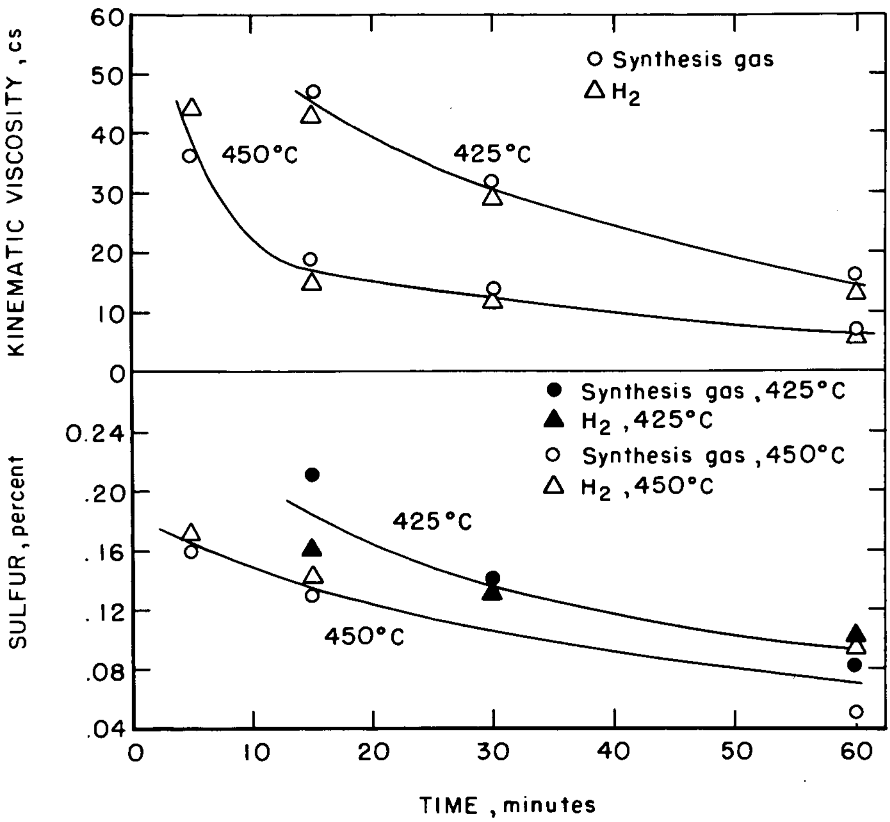

Figure 2 - Kinematic viscosity and sulfur content vs reaction time.

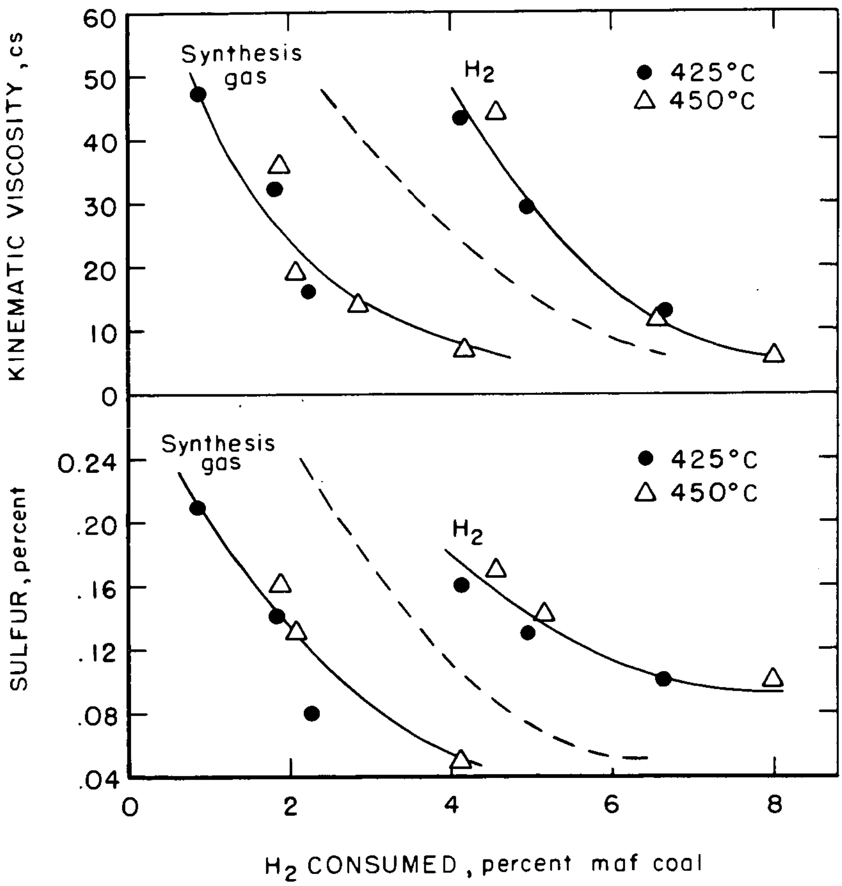

Figure 3 - Change of properties with H_2 consumption.

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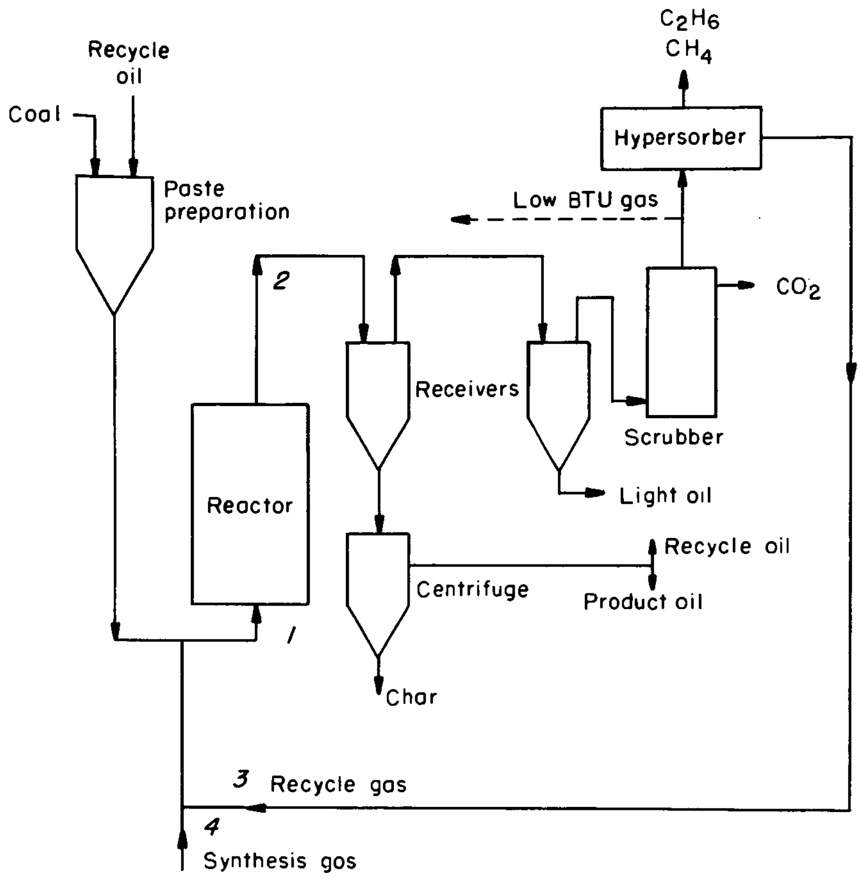

Figure 4 - Flowsheet of conceptual coal liquefaction process using synthesis gas.

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COSTEAM LIQUEFACTION OF LIGNITE

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INTRODUCTION

COSTEAM is a process for liquefying lignite in the presence of added catalysts using synthesis gas as the reducing agent and the moisture in the coal as the source of hydrogen. This development has its roots in the early, largely ignored work of F. Fischer (1). This work was extended at the Bureau of Mines and brought to a point where it now appears to have commercial possibilities (2-5). L. Berg and his group at Montana State University have also reported on coal liquefaction using carbon monoxide (6,7).

The product formed in the early work was too viscous to be easily filtered or used as a vehicle oil for preparing pumpable lignite-oil slurries. The work described here had the objective of replacing the carbon monoxide with lower cost synthesis gas and finding operating conditions where the product is of sufficiently low viscosity to be used as a recycle oil and also be readily filtered.

EQUIPMENT AND PROCEDURES

The experimental work was conducted in a 300-ml stainless steel rocking autoclave. This autoclave required 0.4-0.5 hr to bring the temperature from 300°C, below which little reaction occurred, to the operating temperature. After the desired heating period agitation was stopped. No beneficial reaction was observed after agitation ceased. The reported reaction times do not include heating and cooling times. Product workup included decantation of the free water in the autoclave followed by filtration at about 95°C through a Buchner funnel. The residue was rinsed with benzene. This wash solution was collected separately and stripped free of solvent before adding to the hot filtrate. The conversion is 100% less the percent of residue on a dry, ash-free (maf) basis. The oil yield is the actual recovered yield, also on an maf basis, without correction for mechanical losses.

In experiments studying material balances, the autoclave was weighed on a bullion balance having a sensitivity of 50 mg. This enabled the weight, as well as volume of the gas charged to the autoclave and discharged from the autoclave, to be measured accurately. Material balances better than 98% were obtained.

Unless noted otherwise, North Dakota lignites were used in this work. The laboratory-grind material was prepared by ball milling under nitrogen and then storing under refrigeration until used. The laboratory lignite contained 33% water. The plant-grind material from the Beulah mine was partially dried in air, pulverized in a hammer mill under inert gas, and then put through a bull-ring mill, also under inert gas. Seventy percent of this material was minus 200 mesh. Composition: moisture, 15.4%; ash, 9.5%; Btu's/lb 8930 on an as-received basis. On an maf basis: H, 4.9%; C, 71.2%; N, 1.0%; S, 1.2%; O (by difference), 21.7%; Btu's/lb, 11,890.

The lignite used in most of this work was the laboratory preparation from the Beulah Mine, unless noted otherwise. Twelve grams of this material, on an mf (moisture-free) basis and 28 g of Reilly cut No. 4 anthracene oil were charged to the autoclave, unless noted otherwise.

RESULTS AND DISCUSSION

Effect of Gas Composition. A major change from earlier work in liquefying low rank coals with carbon monoxide and water was the replacement of the carbon monoxide with synthesis gas. This was done not only because of the lower cost of the synthesis gas but because hydrocracking occurs more in the presence of hydrogen than carbon monoxide. Although extensive cracking is not desirable, some is needed to reduce the molecular weight and viscosity of the product. The somewhat higher reactivity of carbon monoxide is counterbalanced by the lower cost of the synthesis gas and by the necessity to increase the extent of cracking sufficiently to obtain a liquid material.

A comparison of hydrogen and carbon monoxide for the hydrogenation of acetophenone (Table 1) shows that carbon monoxide is selective with respect to reduction of the carbonyl group, whereas hydrogen causes more cracking. The high activity of carbon monoxide for reducing carbonyl groups is believed to be the reason that low rank cials are liquefied more readily in the presence of carbon monoxide than hydrogen (1,2). Low rank coals not only contain more carbonyl groups than higher rank coals but also contain the alkaline materials that are converted to formates, the probable active reducing agents (8).

TABLE 1. Reduction of acetophenone

(100 g acetophenone, 25 g water, 5 g Na_2CO_3, 1000 psig initial pressure, 1 hr)

Temp,		Product composition, percent					
°C	Gas	$PhCOCH_3$	$PhCHOHCH_3$	C_6H_6	PhMe	PhEt	Styrene
300	CO	57	43	-	-	-	Trace
300	H_2	98.8	1.2	-	-	-	-
350	CO	55	40	.5	.2	1.6	1.8
350	H_2	92	1.7	3	.1	1.6	0.1
380	CO	54	27	3.2	1.8	6.0	2.0
380	H_2	61	2.3	8.6	5.2	10.5	0.4

Hydrogen becomes more effective in hydrogenating coal as the temperature is increased. The difference in behavior between carbon monoxide and hydrogen decreases as the temperature increases. Nevertheless the data in Table 2 show higher conversion with carbon monoxide at all temperatures, over the range of 375° to 425°C, despite the higher pressures used with hydrogen. The data in Table 2 were obtained in the absence of a solvent in order to keep the conversion low where the differences are large enough to be meaningful.

Table 3 shows quantitative data for the initial gas, product gas, gases consumed and gases generated during a typical run. The moles of carbon oxide gases recovered is slightly lower than the moles charged (98.5% of charged $CO + CO_2$). Experiments using pure hydrogen have shown that some CO_2 is split from the lignite during processing. Some CO_2 may have been lost as a result of reacting with alkaline ash components to form bicarbonates. Some CO may have been converted to methane by hydrogenation promoted by iron in the lignite.

TABLE 2. Effect of temperature on the relative effectiveness of carbon monoxide and hydrogen

(30 g Elkol Mine subbituminous coal, no solvent)

Gas	Water, ml	Pressure, psig Initial	Pressure, psig Maximum	Time, min	Temp, °C	Conversion, percent
CO	15	1500	4200	15	375	43
H_2	None	2500	5400	15	375	27
CO	30	1000	3970	30	400	60
H_2	None	2000	4670	30	400	40
CO	30	1000	4200	30	425	70
H_2	None	2000	4650	30	425	63

TABLE 3. Reducing gas balance

(10.65 g maf lignite, 28 g anthracene oil, 5.9 g H_2O, 0.87:1 H_2:CO, 30 ml autoclave, 0.46:1 weight ratio gas:coal-oil slurry, 4000 psig, 15 min at 450°C)

	Gas in		Gas out		Difference
	1900 psig		1760 psig		140 psig
	1,034 std ft^3		1.010 std ft^3		0.024 std ft^3
Composition:					
	Mole-pct	Gram	Mole-pct	Gram	Gram
H_2	46.73	1.23	47.36	1.22	0.01
CO	51.57	18.88	30.54	10.92	7.97
CO_2	0.10	0.06	19.10	10.73	-10.66[1]
C_1	-	-	1.90	.39	-0.39[1]
C_2	0.20	0.08	0.55	0.21	-0.31[1]
		20.25		23.49	

[1] A negative value indicates weight of gas produced.

Figure 1 shows that as the operating pressure increases it is possible to increase the concentration of hydrogen in synthesis gas and still obtain high conversions. Although 100% hydrogen gave poor results at 420°C in the pressure range investigated, an improvement in conversion was obtained at the higher pressures with relatively small percentages of carbon monoxide in the reducing gas. The high conversions were obtained by using an excess of gas and good agitation in the rocking autoclave. Under conditions where gas-liquid contact is poor, higher pressures are needed to obtain conversions near 90%. The addition of tetralin, a hydrogen donor, increased the conversion but the same improvement was also obtained by increasing the operating pressure a few hundred pounds. Because of the increase of hydrogen activity with temperature, the curves in Figure 1 would be expected to be flatter at higher temperatures and steeper at lower temperatures.

Effect of Temperature. Increasing the temperature causes an increase in gas consumption and a decrease in product viscosity (Figure 2). Based on our experience with recycle operation a viscosity of 50 centistokes (cs) at 60°C was chosen as an upper limit for a desirable product obtained using 12 g of lignite to 28 g anthracene oil. Using this viscosity criterion, Figure 2 indicates that at 3000 psig the minimum operating temperature is about 430°C.

In order to minimize the reaction time necessary for desirable viscosity, temperatures near 450°C are recommended. Table 4 shows that at constant reaction time the product viscosity continues to drop with increased operating temperature but that the oil yield drops significantly. At the shorter contact times possible at the higher temperatures, gas consumption also decreases. The consumption of carbon monoxide is relatively constant with temperature between 450° and 475°C. Most of the increase in gas use is due to greater consumption of hydrogen at the higher temperatures. A breakdown of the gas consumption in Table 4 shows that considerably more hydrogen is formed, via the water-gas shift reaction than is consumed in all but the highest temperature experiments.

TABLE 4. Effect of temperature and time (4000 psig)

Temp, °C	Time, min	Conversion, percent	Oil yield, percent	Kinematic viscosity, cs at 60°C	Gas used, ft^3 CO	Gas used, ft^3 H_2
450	15	96	62	39	.250	-.075[1]
460	15	94	43	36	.229	-.014[1]
475	15	94	42	28	.259	.019
450	3	94	56	52	.221	-.018[1]
460	3	92	53	48	.217	-.010[1]
475	3	94	50	44	.222	.031

[1] Minus figures indicate hydrogen formation.

Effect of Pressure. Table 5 suggests that the minimum operating pressure for obtaining a product of desirable viscosity is 3000 psig. Conversions of lignite are good at all of the conditions listed in Table 5 but the best oil yields and viscosities were obtained at the higher pressures. Gas consumption also increases with pressure. Surprisingly, the extent of cracking to C_1 to C_4 hydrocarbons does not appear to increase significantly with an increase in pressure from 3000 psig to 4000 psig. When the temperature is near 450° C, with about a 15 minutes reaction period, the percent of lignite converted to hydrocarbon gases is 7 to 8% (Table 6).

TABLE 5. Effect of operating pressure (1 hr reaction time)

Operating Temp, °C	Operating Pressure, psig	Conversion, percent	Oil yield, percent	Kinematic viscosity, at 60°C	Gas used, ft^3 $CO + H_2$
430	2000	95	52	79	.186
430	3000	96	55	53	.189
430	4000	98	62	39	.210
450	2000	85	44	76	.186
450	3000	93	54	45	.263
450	4000	96	55	36	.311
460	2000	87	39	73	.187
460	3000	94	48	42	.296
460	4000	94	52	31	.299

TABLE 6. Effect of operating variables on gas production

Temp, °C	Pressure, psig	Time hr	CH_4, gram	C_{2-4}, gram	Lignite gasified,[1] percent
400	3000	1	.15	.18	3.1
425	3000	1	.33	.28	5.7
450	3000	1	.66	.58	12.4
450	3000	.5	.43	.33	7.1
450	3000	.25	.42	.41	7.7
425	4000	1	.30	.29	5.5
450	4000	.5	.52	.37	8.4
450	4000	.25	.43	.34	7.2
450	4000	.05	.32	.25	5.3

[1] To C_1-C_4 hydrocarbons.

Recycle Operation. In order for a potential coal liquefaction process to have commercial possibilities, the product should be capable of being used as a recycle vehicle oil for preparing pumpable coal-oil slurries. In addition, the product oil must have sufficient reactivity or solvency power for coal so that conversions and product viscosities do not deteriorate with extended recycle operation. Table 7 shows that even at the borderline conditions of 3000 psig and 430°C, using fresh lignite, it was possible to use the product oil as solvent in 10 consecutive runs with no signs of inoperability. The initial run used anthracene oil as a solvent and the product from this first run had a kinematic viscosity near 50 centistokes at 60°C. The viscosity increased to 110 cs at 82°C by the completion of the eleventh run where over 90% of the vehicle oil was lignite derived. The viscosity appeared to have leveled and the product filtered readily at about 95°C.

The addition of a small amount of formic acid caused the product viscosity to remain lower. However, improvement in product viscosity can be obtained more inexpensively by modest increases in temperature and/or pressure.

Recycle operation using a sample of lignite that had been in storage about two years, under nitrogen, after being air dried and ball-milled in a drum sized mill showed poor behavior. By the eleventh run, the product was so viscous that it could barely be filtered and the yield of recovered oil was low. Despite the high viscosity of the product from this last run, a not unreasonable conversion of 78% was obtained.

An additional set of experiments was conducted to further evaluate laboratory versus large scale milling of lignite. The data in Table 8 show that if reasonable precautions are taken to prevent oxidation during milling, the pulverized lignite is acceptable as a COSTEAM feedstock. A comparison at two sets of conditions shows very little loss of activity of the plant-grind lignite. A small increase in viscosity and a small increase in gas consumption may have resulted from the air-drying step to which the lignite was subjected prior to grinding under inert gas. This lignite was tested about a month after grinding. The aged plant-grind lignite, however, gave a product of decidely greater viscosity and consumed more total gas. Because of the loss of activity during drying (2), it is recommended that the lignite be dried under inert gas, or if possible, the drying step omitted.

TABLE 7. Liquefaction of lignite using recycle oil

(1 hr 430°C, 1:1 synthesis gas, 3000 psig, H_2O:coal:oil ratio 9:30:70)

	Fresh laboratory-grind lignite[1]				Aged lignite[a]	
	11th Run	Average of 11 runs	11th Run	Average of 11 runs	11th Run	Average of 11 runs
Additive	-----1% HCOOH--------		--------None---------		Water to equal fresh lignite	
Conversion, %	87	90	87	90	78	85
Oil yield, %	55	54	54	56	29	34
Product:						
C	88.6	--	89.8	--	89.5	--
H	7.1	--	6.8	--	6.6	--
N	1.1	--	1.1	--	1.1	--
S	.13	--	.10	--	.12	--
O	3.0	--	3.2	--	2.6	--
Ash	.05	--	.03	--	.04	--
Kinematic viscosity,						
cs at 60°C	190	--	598	--	12,800	--
cs at 82°C	46.8	--	110	--	1,030	--
Btu/lb calcd.	17,056	--	16,886	--	16,906	11

[1] North Dakota lignite (Zap Mine, 29.5% H_2O, 9.0% ash). [a] North Dakota lignite (Beulah Mine, 20.3% H_2O, 7.3% ash), plant-grind.

TABLE 8. Effect of grinding method and lignite aging

(4000 psig, moisture adjusted to 5.9 g for 12 g mf lignite)

Grinding method	Time, hr	Temp, °C	Conversion, percent	Oil yield, percent	Kinematic viscosity, cs at 60°C	Gas used, ft^3 CO	Gas used, ft^3 H_2
Ball mill	.25	450	96	60	30	.223	-.015[1]
Ball mill	1.00	425	95	61	37	.246	.004
Plant-grind	.25	450	96	62	39	.250	-.075[1]
Plant-grind	1.00	425	95	63	39	.245	.003
Plant-grind[a]	1.00	425	96	60	45	.242	.108

[1] Minus figures indicate increase in gas. [a] Aged lignite, stored several years under N_2.

CONCLUSION

Autoclave work has established the feasibility of processing low rank coal, in the absence of added catalysts, to a low-sulfur, low-ash fuel oil, using synthesis gas and moisture in the coal as the source of hydrogen. Using oil yields, product viscosities, and gas consumption as criteria, operating values have been found which can be used as a starting point for larger scale continuous operation studies.

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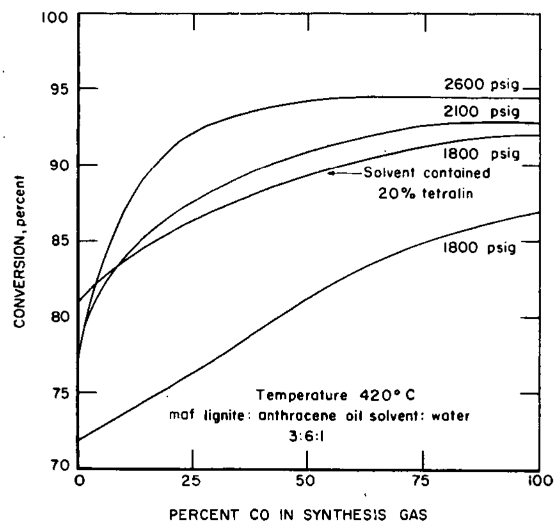

FIGURE 1 - Liquefaction of lignite in autoclave at 420°C.

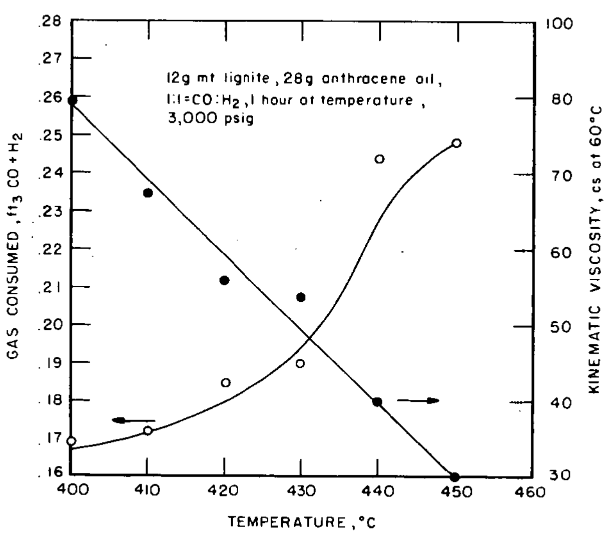

FIGURE 2 - Effect of temperature on gas use and viscosity.

L-14071

A PHOTOMICROGRAPHIC STUDY OF COAL DISSOLUTION

by

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A critical step in several of the processes for production of liquids from coal is the dissolution of coal in a suitable carrier solvent. An example is the noncatalytic solvent refining of coal(SRC) process in which coal is slurried with a solvent and, in the presence of hydrogen gas, heated to 375 - 425°C. Subsequent filtration of the resulting solution and distillation of the solvent leaves a solid (solvent refined coal) low in ash and sulfur, suitable for use as a boiler fuel. The actual dissolution appears to involve both chemical and thermal phenomena, and although it has been shown to be technically feasible, the exact mechanisms and the rate-limiting steps have not been defined clearly.

The highly porous structure of coal suggests that intraparticle mass transfer and diffusion could play a vital role in its dissolution. Likewise, fluid-particle transport phenomena cannot be ruled negligible a-priori. If these effects are appreciable, then the size of the coal particles should be an important operational variable; for, the larger the size of the particles, the longer the diffusional path and the smaller the ratio of external to internal surface area. Typically, however, as reported by Curran et. al.[1] and others[2], the rate of dissolution has been observed to be independent of particle size. A few studies[3,4], on the other hand, show particle size to be a variable of some importance. Additional investigations in this area thus seem warranted.

Hill, et. al.[5] have applied Eyring Absolute Reaction Rate Theory to the kinetics of the dissolution of bituminous coal in tetralin. Average heats of activation and apparent entropies of activation are presented, and marked changes are shown to occur in the entropy of activation as dissolution proceeds. This is interpreted to imply that the fraction of reaction sites available for reaction increases drastically during dissolution. The exact manner and rate of particle break-up to form these additional reaction sites, however, has not been clearly established.

Dryden[6], proposed that dissolution occurs by the removal of units of colloidal size directly from the coal. He maintains that coal consists of a matrix of larger, strongly linked micelles which are intimately associated with smaller, less strongly bonded micelles and that dissolution occurs by removal of these colloidal units, with the smaller micelles dissolving and the larger ones being indestructible at the temperature of dissolution. He explains further that the difference between these two micelles is one of degree rather than kind in that they probably form a continuous series with the dividing line being determined by the temperature. A model similar to Dryden's is given by Hill[5], et. al. with the exception that they consider the idea of an indestructible micelle to be untenable in light of their observation that activation energy increases continuously with dissolution.

Another proposed description for the dissolution of coal, which is completely opposite in concept to Dryden's model, is reflected in A. Gillet's[7] analysis of dissolution at high temperatures (360°C) in hydrocarbon solvents such as anthracene oil and phenanthrene. He hypothesizes that coal dissolves as a unitary substance - like gelatin in water - to form unstable compounds (or complexes) which gradually decompose and that, even when the temperature is maintained constant, a considerable part of the dissolved material is precipitated within a comparatively short time. Lowry[8] appears to have confirmed this hypothesis by observing solutions of coal in tetralin at 300°C to be optically clear when hot, but to become rapidly colloidal when allowed to stand.

Ashbury[3], in his study of benzene pressure extraction of Edenborn coal, also observed percipitation of extract to occur with cooling. Yet, he differed from Gillet's hypothesis by inferring that the extract would remain as a true solution if the temperature were held constant, for his percipitated material redissolved when heated only to 80°C. Assuming that coal extracts are true solutions, Curran[1] et.al. derived a reaction model capable of representing well experimental data for coal dissolution in active hydrogen-donor solvents such as tetralin. Moreover, they state that no evidence exists supporting the formation of colloidal mixtures since the coal extract solutions could be filtered without deposition of extract through a filter with a pore size of only 100 A°.

In light of the above investigations, it appears that some controversy exists regarding the exact mechanism of particle-liquid interaction in the dissolution process. Generally, however, it appears from these earlier studies that particle size is of more importance in the low temperature solvent extraction of coal as opposed to the more complete dissolution obtained using high temperature hydrogen donor solvents. Thus, while it may be surmised that individual coal particles retain their integrity longer in the former processes, quantitative data on this facet of dissolution at high temperatures is lacking. The purpose of this study is to elucidate the mechanism by which individual coal particles dissolve at high temperatures and, thereby, to attempt to resolve and extend some of the observations of earlier investigators. In this belief that visual evidence would be enlightening, this study was based on monitoring the change in particle size at various stages in the coal dissolution process utilizing a previously somewhat neglected technique - that of photomicroscopy. From the evidence obtained in this manner, some conclusions may be drawn regarding the importance of fluid-solid phenomena in coal dissolution, and the applicability of homogenous phase reaction kinetics. In addition, some new insights into the relative roles of gaseous hydrogen versus donor solvent hydrogen are offered.

Experimental

Kentucky No. 9 coal was crushed and sized by screening for use in the experiments. The analysis of the original coal and that of each fraction after screening is shown in Table 1, where the composition of each size fraction is seen to be similar. The -60 +80 fraction was selected for use in the experiments. The solvents used were creosote oil (Table 2) (start-up solvent for the SRC plant at Wilsonville, Alabama), paraffin oil (Will Scientific Co.,) decalin, and tetralin (Eastman Kodak). Hydrogen and nitrogen gases were the 6000 psi grade supplied by Linde. A 6/1 solvent to coal weight ratio was used in all experiments reported here. All coal was dried overnight at 100°C and 25 inches Hg vacuum before use.

An Autoclave Engineers' 300 cc magnedrive autoclave was used as a reactor, with auxiliary equipment for slurry injection and for liquid sampling. The autoclave was equipped with a turbine agitator, baffle, cooling coil, thermowell, and five ports. These ports were used for: (1) rupture disk, (2) slurry injection, (3) gas inlet, (4) liquid sampling, and (5) gas sampling. The autoclave was heated by an electric furnace surrounding the base and controlled by means of a powerstat or automatic controller. Chromel-alumel thermocouples and a Bristol multi-point recorder were used to indicate temperature.

The autoclave was equipped with a cylinder and piston arrangement designed for quick sample injection into solvent preheated to reaction temperature. This injection procedure was used in preliminary experiments with the somewhat surprising result that, at 400°C, all coal particles dissolved before a sample could be withdrawn from the reactor, a time period of about one minute. To alleviate this situation, the injection procedure was replaced by one in which batches of coal and solvent were heated together to a sequence of increasingly higher temperatures. Upon reaching the desired temperature for a particular experiment, the resulting mixture was immediately quenched to room temperature, a Soxhlet extraction with acetone was performed and a photomicrograph at 50X was made of the residue remaining in the Soxhlet thimble.

To insure that only individual coal particles were photographed, the residue was treated in an ultrasonic bath to disperse all agglomerates. The slide mounting medium used was Araclor 5442, a thermoplastic resin produced by Monsanto. Several drops of Araclor, heated to above its melting point was dropped onto a slide, smeared out, and allowed to become tacky. A drop of the residue dispersed in acetone was then dropped onto the Araclor on the slide which then was placed on a hot plate until the Araclor remelted. Finally, the particles were dispersed in the Araclor by stirring with a toothpick, the dispersion covered with a coverglass, and allowed to cool and harden. The slide was examined under the microscope for areas of good dispersion and photographs were made of those areas. A Leitz Panphot Photomicrograph equipped with a Polaroid 4x5 film holder was used for particle size comparison. Further details concerning the above procedures are given by Green[9].

Results and Discussion

Experiments were conducted to explore the roles of temperature, hydrogen donor activity, and gas phase composition upon the dissolution of coal. All three variables were found to have significant effects. The results from this work do not establish whether coal dissolves forming a true solution and partially re-precipitates during analysis or whether it simply fragments into smaller units during the initial stages of dissolution. It is likely that a combination of these two mechanisms actually takes place. For this reason, the term disintegration is introduced to represent the overall process by which the smaller particles are formed.

Effect of Temperature

From Figures 1a - f, it is obvious that temperature plays a highly significant role in the dissolution process. No apparent disintegration of the coal particles occurs until a temperature of 340°C is reached, at which time fragmentation begins. At 350°C considerable disintegration has taken place and no original coal particles remain intact. At 360°C disintegration appears complete and, in fact, additional reaction at 400°C for two hours produces no further changes in physical appearance as shown in Figure 1f.

These results appear to explain the marked changes in apparent entropy of activation observed by Hill[5], which can be attributed to a sudden increase in available reaction sites. Such an increase is in line with the speed of coal disintegration observed here. The fact that particle disintegration occurs almost instantly once a temperature of about 350°C is reached also shows why injection type experiments, in which samples could be collected at a minimum of two minute intervals, were unsuccessful for monitoring the extent of particle break-up. Heat transfer calculations[10] give the time required for a 0.2 mm diameter coal particle to reach the solvent temperature after injection as only about 0.2 sec and hence the disintegration occurs so rapidly, once a high enough temperature is reached, it is reasonable to conjecture that the thermally activated reaction is controlled by the heat transfer rate to the particle, which is very fast for the small particles used here. As seen from Figure 1, a high activation energy is required for disintegration, as implied by the drastic changes occuring with the relatively small changes in temperature from 330 to 340°C and from 340 to 350°C.

It is very interesting to note that in each of the experiments represented in Figure 1, the amount of acetone solubles as determined by Soxhlet extraction remained very low (less than 10 per cent) despite the drastic changes in particle size. Figure 2 indicates how the yield based on acetone solubles changes with reaction time, with the yield of 50 per cent at two hours corresponding to the photomicrograph given in Figure 1F. Thus, we can conclude that the yield measured by Soxhlet extraction tests is not directly related to the early dissolution of the solid coal particles. At these early stages, it appears that a significant fraction of the coal already dissolved re-precipitates during the Soxhlet extraction. This is supported by the fact that the acetone insoluble residue remains at the same size despite the length of reaction time. Further evidence is provided by the photomicrographs given in Figure 3, obtained using a scanning electron microscope. The particles appear to be of uniform size and have a globular appearance as would be expected with re-precipitated material. The large particles in Figure 3 are assumed to be mineral matter, this is presently being verified.

These observations and implications raise some question as to the significance of obtaining reaction kinetics using acetone insolubles (or as more commonly reported, benzene insolubles). If a true solution is formed once a sufficiently high temperature is reached, as proposed by Gillet[7] and inferred above, benzene insolubles, as currently determined, probably do not represent conditions existing at the reaction temperature and pressure. The relationship between insolubles and actual dissolution is thus somewhat obscure. Yet, this measure is often used as the characteristic parameter in treating the kinetics of dissolution and is typically assumed to correlate well with the degree of depolymerization of the coal. Since additional reactions and considerable precipitation of coal extract may occur while determining Soxhlet insolubles, some doubt may arise as to the meaning of a kinetic treatment of dissolution based on benzene insolubles, and this matter should be the subject of further investigation. In any event, it does appear that a distinction must be made between the amount of MAF coal undissolved at reaction conditions and the amount of insolubles as determined by Soxhlet extraction.

Effect of Hydrogen Donor Activity

While the above sequence has shown dissolution to be a thermally activated process, these further experiments show that application of heat alone is insufficient to disintegrate the coal particles in the temperature range used here. Rather, these photomicrographs show that hydrogen transfer is a necessary prerequisite for disintegration.

The effect of four different solvents having varying hydrogen donor capacities is shown in Figures 4a-e. All four reactions were conducted for two hours at 400°C in their respective solvents. Tetralin and creosote oil, the best hydrogen donors, disintegrate the coal effectively, while paraffin oil, which donates little hydrogen, has virtually no effect on the coal. Decalin is an intermediate strength hydrogen donor. Curran[1] et. al. for instance, report only 0.28 per cent hydrogen transfer to MAF coal using decalin as opposed to 1.21 per cent with tetralin. From Figure 4c it is observed that the coal only partially disintegrates in decalin. Thus, a direct correlation exists between coal disintegration and hydrogen donor activity of the solvent.

From the results in paraffin oil, it is obvious that the application of heat alone at 400°C is insufficient to disintegrate the coal particles, while disintegration occurs readily at that same temperature with a solvent capable of providing sufficient hydrogen, as exemplified by the tetralin and anthracene oil results. Apparently then, disintegration occurs as a fast fluid-solid hydrogenation surface reaction having a high activation energy. In processes such as the solvent refining of coal, therefore, the liquefaction stage should be treated as a chemical process rather than as a strictly thermal process as in pyrolysis.

Effect of Gas Phase Composition

Often in coal liquefaction operations supplemental gaseous hydrogen is added to the solvent-coal slurry; however, little information is available as to the relation between hydrogen transfer from a donor solvent versus that from gaseous hydrogen. The experimental results of Figure 5 clearly show that hydrogen may be donated directly to coal particles in the absence of a donor solvent and that this will result in particle disintegration, although at a somewhat slower rate than when a donor solvent is present. Here, the rate of disintegration may be limited by intraparticle diffusion of dissolved hydrogen gas in the liquid filled pores. Such diffusion would be unnecessary were the pores filled with a solvent capable of donating hydrogen directly. The necessity for providing some form of hydrogen for particle disintegration is apparent from the negative results in Figure 4d,obtained using a nitrogen atmosphere with paraffin oil as a solvent.

Conclusions

From this photomicrographic study, it can be concluded that the disintegration of coal particles in a hydrogen donor solvent occurs almost instantaneously at 360°C, although the application of heat alone is insufficient to render the particles soluble at this temperature. The necessary hydrogen for disintegration may be provided also by molecular hydrogen as a dissolved gas, although perhaps at a slightly slower rate than from a donor solvent. The rapidity of particle disintegration suggests that heat transfer to the particle may be rate controlling, although this would be unimportant from a practical processing standpoint. It appears that a direct relationship between particle dissolution and insolubles from Soxhlet extractions is difficult to ascertain, because of the possibility of reprecipitation of dissolved coal species. These results also indicate that hydrogenation and hydrodesulfurization take place on a much longer time scale than particle disintegration and that these two processes may be regarded as occuring in a homogenous liquid phase, rather than as a fluid-solid surface reaction of the type present in hydrogasification. The speed with which particle disintegration occurs partly explains the lack of importance placed upon initial particle size and agitation rate in non-catalytic coal liquefaction processes.

Acknowledgement

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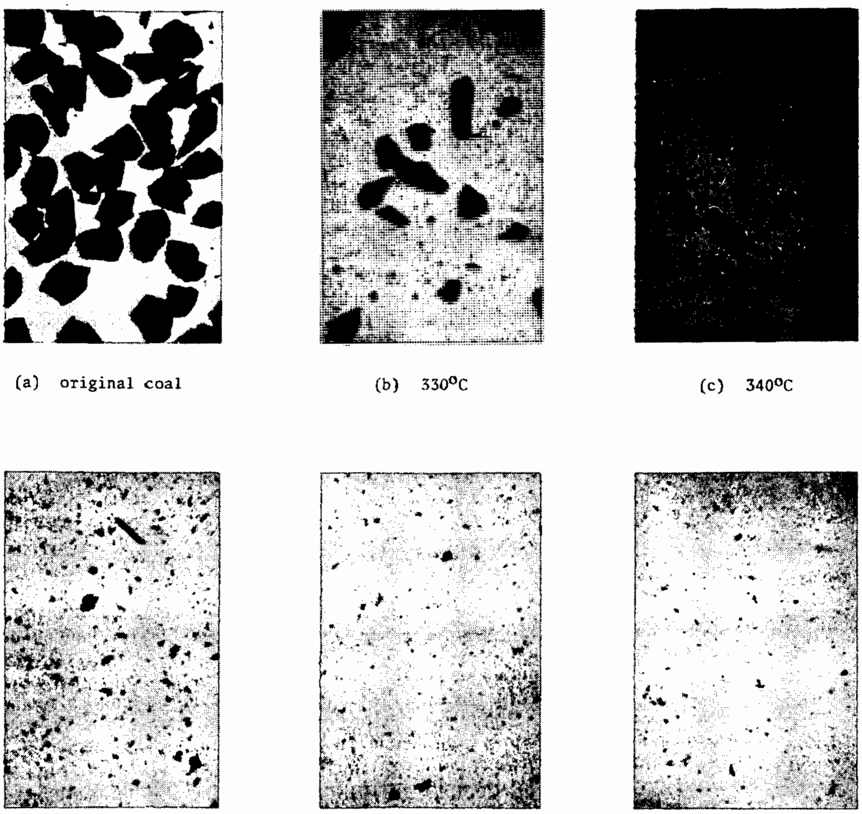


(a) original coal

(b) 330°C

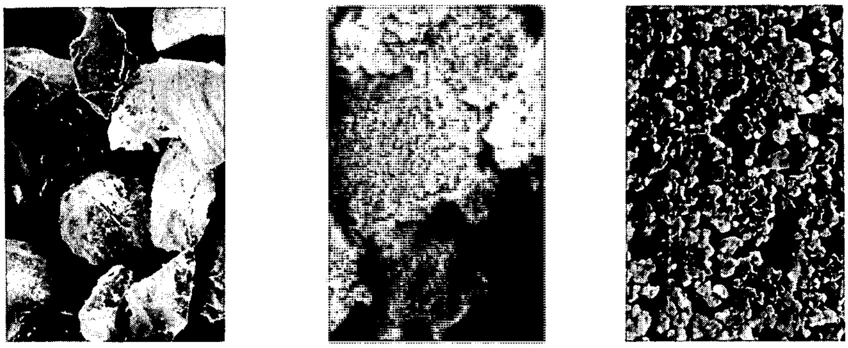
(c) 340°C

(d) 350°C

(e) 360°C

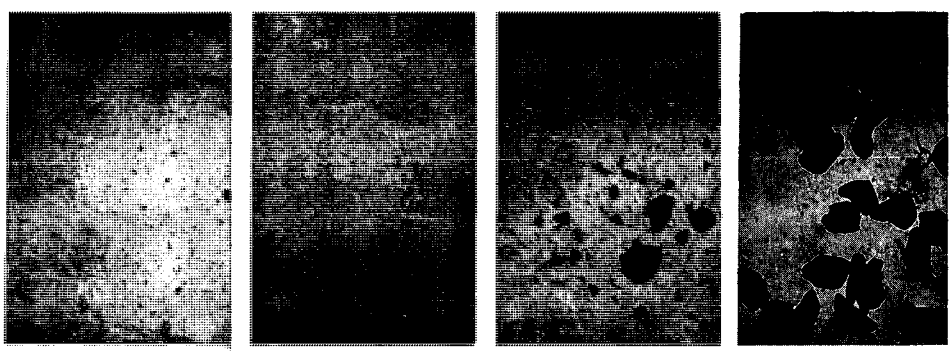
(f) 400°C, 2 hours

Figure 1: Effect of temperature on the disintegration of -60 +80 mesh coal particles using creosote oil and hydrogen atmosphere



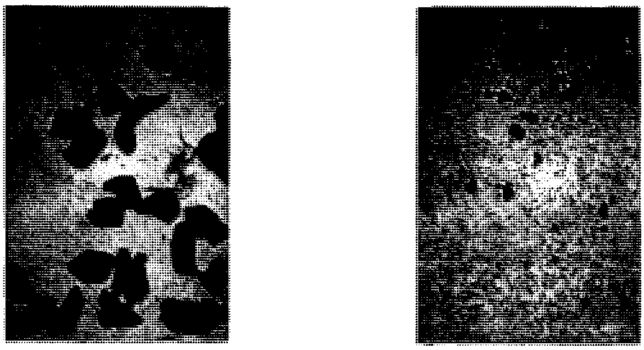
(a) original coal particles, 100x (b) Soxhlet residue, 500x (c) Soxhlet residue, 1000x

Figure 3: Residue from Soxhlet Acetone Extraction after dissolution in creosote oil and hydrogen gas at 360°C



(a) creosote oil (b) tetralin (c) decalin (d) paraffin oil

Figure 4: Effect of solvent hydrogen donor activity on particle disintegration after 2 hours at 400°C with nitrogen atmosphere



(a) nitrogen atmosphere (b) hydrogen atmosphere

Figure 5: Effect of gas phase composition on particle disintegration at 400°C after 2 hours in paraffin oil

TABLE 1

ANALYSIS OF KENTUCKY NO. 9 COAL AND SIZE FRACTIONS

FRACTION	ASH Moisture Free %	Carbon %	ULTIMATE Hydrogen %	ANALYSIS(MAF) Nitrogen %	Sulfur %
Original	10.2	77.8	6.4	1.5	3.8
-25 +35	9.8	77.4	6.6	1.5	4.2
-35 +45	9.6	77.4	6.4	1.4	3.8
-45 +60	8.8	78.0	6.8	1.3	3.8
-60 +80	9.0	76.0	5.6	1.2	3.8
-80 +120	8.5	73.5	5.7	1.2	3.7
-120 +170	8.4	74.4	5.4	1.2	3.6
-170 +230	7.3	76.1	6.3	1.5	3.8
-230 +325	9.1	85.6	5.8	1.6	4.2
-325 +400	9.5	86.8	5.9	1.6	4.0
-400	10.6	74.3	5.4	1.4	4.5

Table 2

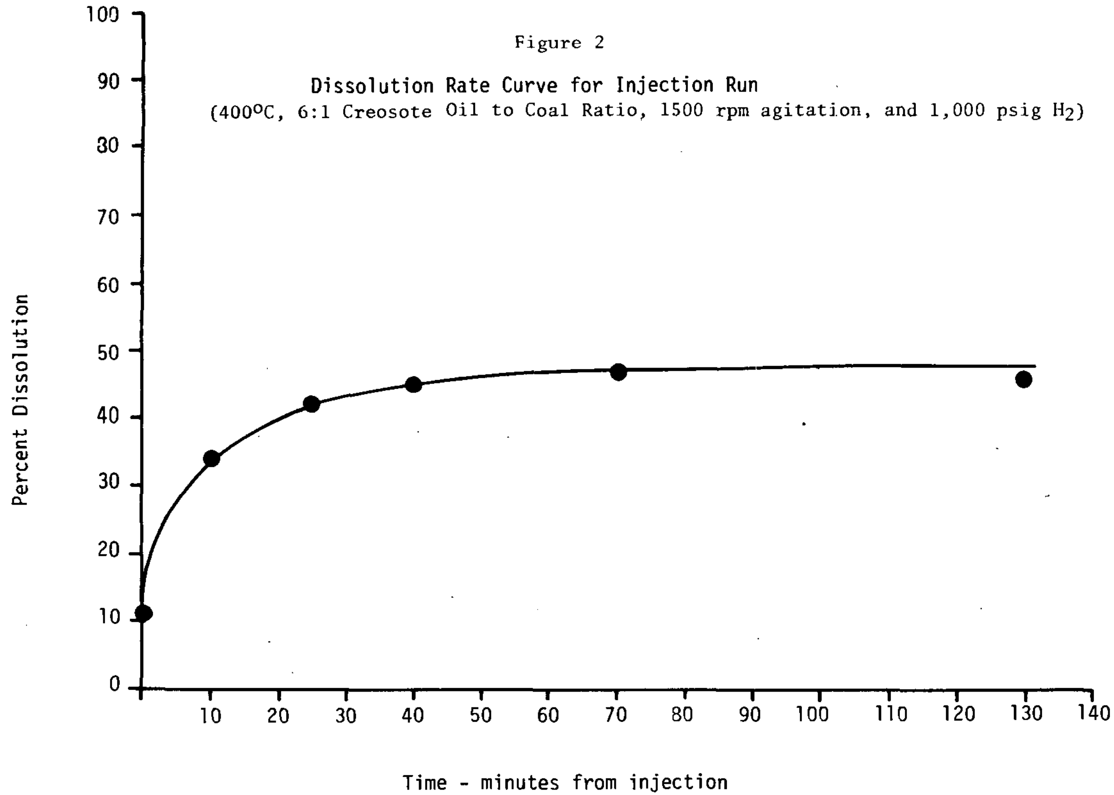
MAJOR COMPONENTS IN CREOSOTE OIL

Naphthalene	10%
2-Methylnaphthalene	8%
1-Methylnaphthalene	3%
1,2-Dimethylnapthalene	9%
Acenaphthalene	5%
Fluorene	5%
Anthracene and Phenanthrene	17%
Carbazole, Fluoranthene, Pyrene	5%
Other(about 30 identified)	38%
TOTAL	100%

Figure 2

Dissolution Rate Curve for Injection Run

(400°C, 6:1 Creosote Oil to Coal Ratio, 1500 rpm agitation, and 1,000 psig H_2)



DEASHING OF COAL LIQUEFACTION PRODUCTS VIA PARTIAL DEASPHALTING. I - HYDROGEN-DONOR EXTRACTION EFFLUENTS

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INTRODUCTION

One of the more important problems to be resolved in the commercial development of coal liquefaction processes is that of deashing and solids separation.

An extensive laboratory program in a joint program with the Standard Oil Company of Ohio was carried out in the Research Division of Consolidation Coal Company in the period 1959 through 1963 to study the basic essentials of the hydrogen-donor extraction process. The major method of solids separation studied during this period was pressure filtration. The small scale of the experimental work, i.e., maximum feed rate of about 30 lb/hr, precluded the use of continuous filtration equipment. Consequently, all the work was conducted in batch cyclic equipment.

The experimental work was continued and expanded with the financial support of the Office of Coal Research.[1] One of the items covered in the OCR funded laboratory program[1] was further investigation of pressure precoat filtration. Filtration rates were "optimized" and relative freedom from filter blinding was secured by operating in the 500-600°F range. It was noted that some precipitation of dissolved extract occurred in this temperature range.

The OCR funded program culminated in the design and operation of a 20 TPD plant in Cresap, West Virginia.[2,3] The design of the pilot plant, based on prior laboratory data, included the use of continuous pressure precoat filters for solids separation. Mechanical difficulties, which were unresolved, precluded successful operation of the filter system. Filtration rates observed, however, were in the range predicted from prior laboratory data.

The filters were accordingly replaced by a hydroclone system which operated in the range of 500-600°F. Successful operation of the hydroclone system was achieved and the results have been reported.[3] Success was, no doubt, due in part to partial extract precipitation and resulting solids agglomeration on cooling the extraction effluent.

Batch laboratory experiments were conducted prior to operation of the Cresap pilot plant[1,4] on the deashing of extraction effluents by means of the addition of deasphalting solvents.

Laboratory experimentation has continued in both batch and continuous units on improvement of the deashing process. Some of this work has been previously reported[5] where the preliminary results of deashing by continuous settling were presented.

The present paper is concerned with a more detailed account of the above work on deashing.

EXPERIMENTAL

Batch experiments on deashing with deasphalting were conducted in a one-gallon stirred autoclave, 5" I.D. x 12" high. The autoclave was equipped with an adjustable sample probe and a N_2 purged differential cell with the probe functioning as the high-side of the D/P cell. In combination, the probe and the D/P cell could be used to find the liquid-gas interface within the autoclave. Once the interface was found, the probe was moved a prescribed depth into the liquid bed at which point small samples were taken at various time intervals to determine the settling rate of the interface between the settling solids and the clear liquid phase. As a result of the liquid samples withdrawn, there was a net decrease in the level of the gas-liquid interface. A height adjustment was used after each sample to maintain a constant immersion.

The experimental procedure involved stirring the autoclave contents at 890 r.p.m., heating to extraction temperature, holding for prescribed time at temperature, cooling to deashing temperature followed by addition of deashing solvent, if any. At this point the stirrer was stopped and the autoclave contents were allowed to settle.

Samples were taken immediately after stirring was stopped according to a prescribed time and depth schedule. The purpose, of course, was to determine the settling rate. A correction had to be applied in determining the settling rate to account for the perturbation induced by the unavoidable relatively large sample taken for analysis. The correction procedure was checked by applying it to a model system of coal settling in decane where the settling rate could be determined by visual observation.

The continuous unit used for continuous deashing is schematically illustrated in Figure 1. The extraction system itself is adapted to operation at slurry feed rates up to 30 lb/hr. The five-stage extractor contains a total inventory of 1.7 gallons. The construction and operation of the continuous extraction system has been previously described in detail.(2) The operation of the continuous settler without deasphalting solvent addition was also previously described.(5)

The flow sheet of Figure 1 also shows the system for continuous metering of additives to promote deashing. Two types of additives were used. The first consisted of n-decane which acted as a deasphalting solvent. The second consisted of 16% aqueous H_2SO_4. The purpose of the sulfuric acid was to remove soluble alkaline ash from the extract by conversion to sulfates. The stoichiometric feed rate was calculated based on conversion of the combined Na, K, Mg and Ca content of the feed coal to the corresponding sulfates. The extraction effluent is continuously mixed with the deasphalting solvent in the additive contactor. This is a one-gallon stirred, electrically heated vessel usually operated at the same temperature as the continuous settler. The contactor vessel was employed to precool the slurry feed to settler temperature in most cases, even when no additive was used.

A number of different size vessels were used for continuous settling in order to determine the effects of varying throughput rates in lb/hr-ft^2, and of different residence times in the compaction zone below the feed inlet.

The dimensions of the settlers used are outlined in the table below.

Settler No.	ID in	Area, ft^2 Above Feed Point	Area, ft^2 Below Feed Point	Vol. Below Feed Point ft^3
1	7.98	0.328	0.347	0.405
2	4.60	0.096	0.116	0.135
3	4.60	0.096	0.116	0.251
4	3.15	0.045	0.054	0.117
5	3.15	0.045	0.054	0.179

The bottom two inches of the settlers were agitated by a rake rotating at 1-2 r.p.m. The bottom of the rake contained two perpendicular rows of 1/8-inch spikes.

A run was conducted by setting the coal slurry feed composition and rate, extraction temperature, additive feed rate and settler temperature at the prescribed values. The rate of withdrawal of underflow from the settler was also prescribed in advance. The underflow rate was controlled manually by intermittent withdrawal through a 1/2-inch gate valve at 10 minute intervals into the underflow product receiver which was positioned on a weigh scale.

Steady operating conditions were achieved usually after three inventory changes through the system. A material balance period ensued in which samples of all liquid and gas streams were taken. Duplicate gas samples were normally taken at the beginning and end of the material balance period. The methods of analysis and calculational procedures were substantially the same as those previously described.[2]

A number of different coals were investigated including Pittsburgh Seam and Illinois No. 6 coals from the eastern-half of the United States and bituminous and subbituminous coals from the western part of the country. The detailed investigation was, however, confined to two coals, i.e., a Pittsburgh No. 8, a high-volatile bituminous C coal from the Ireland Mine of Northern West Virginia and a Utah subbituminous coal from the Browning Mine in Emery County. Only the work with the latter two coals will be described. Inspections of the two coals are given in Table I. Two batches of the Browning Mine coal were used. As noted, the second batch was significantly lower in sulfur content.

The Ireland coal is a strongly caking, highly fluid and highly caking bituminous coal. The Browning Mine coal is, however, substantially noncaking and exhibits little or no fluidity in the standard Gieseler plastometer test. Its classification by the ASTM system is borderline between high-volatile C bituminous and subbituminous B. Because of its noncaking properties, it is more logical to regard it as a subbituminous coal in rank.

The work with the Ireland coal was conducted with solvents derived from the Cresap pilot plant.[3] These were "natural oils" derived from hydrocracking of the extract in the ebullated-bed catalytic hydrocracker. The oils were of two types, namely, fresh make-up hydro oils derived from the hydrocracker and extraction recycle oils. The latter oils were derived from the make-up hydro oil by recycle through the extraction unit and naturally were more depleted in hydrogen donors than the former. They also contained some undisplaced start-up solvent which consisted mostly of mixed methylnaphthalenes. Analysis of typical oils of this type are given in Table II. The identification of specific compounds by gas chromatographic analysis is somewhat tentative due to the complex nature of the mixture.

The work with the Browning Mine coal on the other hand was conducted mostly with synthetic solvents consisting of mixtures of methylnaphthalene and tetralin.

The definitions given below are applicable to the discussion presented in the remainder of this paper.

Extract in what follows is defined as that portion of the extraction effluent which boils above 240°C at 1 mm Hg and which is soluble in boiling cresol.

MAF extraction residue is the moisture and ash-free portion of the extraction effluent which is insoluble in boiling cresol.

Coal conversion is defined as

$$100 - \frac{100 \text{ lb MAF extraction residue}}{\text{lb MAF coal feed}}$$

Hydrogen transfer in the runs with synthetic solvents is determined as previously[1] from the amount of naphthalene produced via the reaction,

$$\text{tetralin} + \text{coal} \rightarrow \text{coal derived products} + \text{naphthalene}.$$

RESULTS AND EFFECTS OF VARIABLES

A. Ireland Mine Coal

1. Batch Results

A brief summary of the batch results will be given for comparison with continuous results. The average results of a series of runs with natural solvents are given in Table III. Two types of solvent mixtures were used, i.e., 25% Cresap hydro oil-75% recycle oil and 100% hydro oil. No deasphalting solvent was used in these runs. It is clear that a relatively high settling rate can be achieved without addition of a deasphalting solvent. The settling rate is drastically reduced, however, when the coal conversion is increased to 86% by use of 100% hydro oil.

The addition of deasphalting solvents was also studied previously[1,4] in batch experiments. Their effect on settling rates had not been determined. These experiments focused on a determination of the ash content of the clarified extract. All deasphalting solvents used were saturated hydrocarbons and all were effective in reducing ash content of the clarified extract. On a weight basis, all hydrocarbons tried, i.e., n-paraffins, n-butane through n-decane, cyclohexane and decalin were approximately equally effective in deasphalting and reducing extract ash. Their relative effect on rate of settling still remains to be determined, however, and such measurements are now in progress.

2. Continuous Results

The deashing of the extraction effluents from donor extraction using natural "Cresap" derived solvents via gravity settling was investigated in some detail. The products from four extraction conditions were used in this study. The conditions used and a summary of results are given in Table IV.

A series of settling runs were conducted using the effluent from Condition A (1.5 S/C ratio, 75-80% coal conversion) using settling temperatures of 550-600-650°F. No usable data were obtained at 550°F since massive deposits were formed in the settler walls. The settler was clean, however, at the two higher temperatures. The overflow rate in $lb/hr\text{-}ft^2$ was varied over a wide range by use of settlers with various cross-section areas as explained earlier. The underflow rate was not treated as a separate variable. In most runs, it was arbitrarily set at 20% of the feed rate to extraction. This usually gave an underflow stream containing 45-55 wt. % cresol-insolubles.

The effect of the throughput rate on percent ash breakthrough from these experiments is illustrated in Figure 2.

The effect of varying extraction conditions on settling behavior was also studied and results are summarized in Table V. A few runs are also shown in Table V, illustrating the removal of fine ash by sulfuric acid addition.

It is immediately noted that the settler throughput rate can be greatly increased, without sacrifice of deashing efficiency, by increase of the solvent-to-coal ratio from 1.5 to 2.

As was noted previously in batch results, increase of coal conversion from 77 to 86% greatly decreased deashing efficiency at 1.5/1.0 solvent coal ratio. It appeared to have little affect, however, when the solvent-to-coal ratio was increased to 2.

The effect of sulfuric acid addition is largely to reduce the fine ash of the extract. About one-third of the fine ash is removed, largely by conversion of soluble Ca to insoluble $CaSO_4$. About 50% of the extract calcium is removed by sulfuric acid addition.

The extract recovery in the overflow is given in the last row of Table V. It is seen that the extract recovery in the overflow is in the range of 84-88%. Higher recoveries, of course, can be achieved by washing the underflow with feed solvent. Recoveries are also increased, without washing, by increasing coal conversion, increasing the solvent-to-coal ratio and by decreasing the amount of precipitated extract. The above statements follow from the material balance relationships in the system.

A small fraction of the extract is precipitated on cooling the extraction effluent to settler temperatures.

The amount of precipitated extract may be readily calculated from the observed extract-to-solvent ratios of the overflow and underflow streams, if it is assumed that all of the precipitated extract is in the underflow stream. The relationship is

$$X = (E_o/S_o) \Big/ (E_u/S_u) \qquad (1)$$

where:

X = the fraction of underflow extract which is in the soluble form.

$E_{o(u)}$ = lb of extract in overflow (underflow).

$S_{o(u)}$ = lb of solvent in overflow (underflow).

The fraction of total extract precipitated is then readily calculated by material balance.

Equation (1) was applied to the series of runs conducted at 600°F settler temperature at the two solvent-to-coal ratios, respectively, with results as shown below:

Solvent-to-Coal Ratio	No. of Runs	Average Quantity Extract Precipitated, Wt. % MAF Coal	Standard Deviation
1.5	14	2.3	1.5
2.0	3	5.5	1.2

The precipitated extract, was shown by solvent fractionation analysis, to consist, as expected, of the highest molecular weight fraction of the extract, i.e., the benzene insolubles.

B. Browning Mine Coal

1. Batch Results

The batch experiments are summarized in Table VI. It is noted that in contrast to Ireland coal that the settling rate in the absence of additives was very slow. The addition of decane, however, was effective in providing acceptable settling rates.

Synthetic solvents consisting of methylnaphthalene alone or in admixture with tetralin were used. The viscosity of these solvents is lower than that of the higher boiling natural solvents such that the poor settling behavior with the Browning Mine coal cannot be ascribed to use of the synthetic solvent. An experiment in which the Cresap natural extraction solvent was used confirmed again the slow settling rate for this coal in the absence of additives.

2. Continuous Results

The general extraction behavior of the Browning Mine coal in the continuous unit was assayed at the same time that the behavior of deashing via continuous settling was explored. Synthetic solvents, i.e., methylnaphthalene-tetralin mixtures, were used in this work with the tetralin content of the feed solvent varied between 0 and 50%. The temperature was varied between 750-780°F and the solvent-to-coal ratio between 1.5 to 4.0 in this work.

The relationship between coal conversion and hydrogen transfer is shown in Figure 3. Like the results reported previously with Ireland Mine coal,[5] the experimental values fall on a relatively smooth curve independent of the experimental conditions.

Hydrogen transfer in these experiments is defined as the amount of hydrogen transferred to the coal via the general process,

$$\text{tetralin} + \text{coal} \rightarrow \text{coal products} + \text{naphthalene}.$$

A small amount of naphthalene is also produced via hydrogen-donor cracking of the solvent, i.e., by the reaction,

$$1/2\ (\text{tetralin}) + \text{methylnaphthalene} = \text{methane} + 3/2\ (\text{naphthalene}).$$

The naphthalene produced by the second reaction accordingly is excluded from that produced by the first reaction in calculating the amount of hydrogen transfer to the coal.

A kinetic relationship between the rate of hydrogen transfer and the extraction conditions as well as the tetralin content of the solvent was derived and previously presented.[5,6] The relationship was based on the extensive data with Ireland coal. It is interesting to note, that the rate of hydrogen transfer calculated using kinetic constants derived for Ireland coal, closely predicted the hydrogen transfer rates for Emery coal. This is illustrated by Figure 4. It should be emphasized, however, that the coal conversion versus hydrogen transfer relationship is very different for the two coals, i.e., a much higher coal conversion is achieved with the Ireland coal with the same amount of hydrogen transfer.

The exploratory survey of the variables in the continuous unit confirmed the need for addition of decane to achieve a high throughput rate in the continuous settler.

A survey of the effect of temperature and decane addition rates on deashing efficiency was made at 500, 600, and 650°F. The results of the 500 and 600°F runs are shown in Figure 5. No usable results were obtained at 650°F due to coke formation in the conditioner vessel. Thus, like the previous case of Ireland Mine coal without additives, the optimum settling temperature is near 600°F. The operability relationships versus temperature appear to be quite different for the two coals, however. The reason for the difference is not apparent.

Further details on some of the runs conducted with varying decane rates are given in Table VII.

The amount of extract precipitated was calculated by the procedure described earlier for the Ireland Mine coal case for continuous runs which were conducted over long operating periods, i.e., greater than 50 hours, to demonstrate operability. The results are indicated below:

Run No.	Conversion, Wt. % MAF Coal	Decane-to-Solvent Ratio	Wt. % Extract Precipitated
41	36	0.065	0
44	53.7	0.112	2.7
51	63.8	0.290	7.7

The runs in Table VIII are not included because of their short duration and accordingly less accurate material balances.

The extract recovery in Run 51, which was conducted under nominally the same conditions as Run 45-5 gave an extract recovery of 79%.

Experiments were conducted to recover "liquid" extract in the underflow by mixing the underflow with a portion of the extraction solvent and all of the feed decane, and passing the mixture through the settler again. Details have been previously presented,[7] and it was shown that 95% of the "liquid", i.e., unprecipitated extract, was recovered by this technique which simulates a two-stage continuous settler with back washing of the underflow from the first stage.

DISCUSSION OF RESULTS

Ireland Mine Coal

Batch settling may be regarded as proceeding through a hindered settling mechanism, i.e., where the settling rate is equivalent to the fluidization velocity of the given particle size distribution at a given level of compaction. For this reason, the initial settling rate is the highest and the rate decreases as the bed compacts.

The area required in a continuous settler can be approximated from batch results by the familiar "idealized" design equation[8] which is simply derived from material balance considerations:

$$A = \frac{Q\ (F - D)}{\rho\ R} \qquad (2)$$

where:

A = area required to produce clear overflow with underflow composition D and feed composition F.

D = $\frac{\text{weight of liquid}}{\text{weight of solids}}$ in underflow.

F = $\frac{\text{weight of liquid}}{\text{weight of solids}}$ in feed.

ρ = density of the liquid.

Q = solids feed rate.

R = rate of settling of slurry.

There is some uncertainty about the determination of R, but as a first approximation it should equal the initial settling rate of the feed slurry as determined from batch experiments.

Equation (2) should be valid as long as sufficient residence time is provided below the feed point to allow compaction of the underflow to the "material balance" concentration by hindered settling. In all of our experiments, with one exception, sufficient residence time was supplied to achieve the desired level of compaction. From this result, it was determined that the residence time required for compaction to 50% solids is less than 1.7 hours.

Equation (2) implies a sharp breakthrough of solids as upflow velocity in the settler is increased. Experimentally, as the results given in Figure 2 show, this is far from the case, i.e., there is a gradual increase in solids breakthrough as throughput is increased.

The experimental results at 600°F shown in Figure 2 were correlated by the empirical equation of the type,

$$Y = y_o e^{KV/V_o} \qquad (3)$$

where: Y = the percent of the ash reporting to the overflow.
V = the actual upflow velocity of the overflow stream in in/min.
V_o = initial settling velocity of feed slurry, in/min.
y_o and K are arbitrary constants.

For the particular slurry used, S/C = 1.5, condition A, the empirical equation, determined as best fit to the data by the method of least squares takes the form,

$$Y = 1.106\ e^{0.940\ V} = 1.106\ e^{1.88\ V/V_o} \qquad (4)$$

Thus, based on equation (4), if one operates the settler at an upflow velocity equal to the initial settling velocity as determined from batch experiments, one would obtain 93% of ash removal to the underflow. Accordingly, if one desires more efficient ash removal, the velocity must be reduced significantly below the initial settling velocity.

The settling behavior also has to be rationalized with respect to the size consist of the solids in the extraction effluent. These were determined by the Coulter counter method but only after dispersion of the residue particles in tetrahydrofuran. The extract is completely soluble in tetrahydrofuran and thus any particles agglomerated by precipitated extract are redispersed.

The results for two series of runs, i.e., at 76% and 85% conversion levels, respectively, are given in Figure 6. The median particle size is quite small, i.e., 28 and 16 microns, respectively. The higher conversion runs showed a small median particle size which is consistent with the lower settling rate for these extraction effluents.

Figure 7 illustrates the removal efficiency of residue particles as a function of size with the relative velocity V/V_o as parameter. It is noted that high efficiencies of collection of the +10 micron particles can be achieved at velocities up to V_o. Higher velocities cause a rapid decrease in efficiency of particle collection.

The reason for the relatively high rate of clarification remains to be discussed. The terminal velocities at settler operating conditions, for the median and 75% particle sizes were calculated by Stokes law. The densities and viscosities of the various materials used in these calculations were taken from correlations previously reported.(3) The results are shown in Table VIII.

It is immediately apparent, that efficient capture is achieved for many of the particles at upflow velocities greatly exceeding the terminal velocity. Part of this phenomenon is due to the capture or "trapping" of fine particles by the aggregate of particles in the "hindered" settling system. Experiments in model systems of fine Ireland coal dispersed and settling in hydrocarbons confirmed this phenomenon. However, the rate of settling of these slurries was considerably slower than that of the extraction effluents having similar nominal particle size distribution.

It is concluded that to a considerable degree, the high rate of settling is attributable to the agglomeration of the fine residue particles with the precipitated extract behaving as the "binder". The higher settling rate of the 2/1 versus the 1.5/1, solvent-to-coal ratio slurries, is consistent with this assumption and the observation that a higher percentage of extract is precipitated on cooling the higher solvent-to-coal ratio slurries.

Incidentally, the apparent anomaly of lower extract solubility at higher solvent/extract ratios is consistent with earlier measurements.[1]

Browning Mine Coal

The deashing results of the continuous operations, as in the previous case of Ireland coal, are consistent with the batch data, as can be seen by comparison of data in Tables VI and VII.

Particle size distribution of extraction residue for the Browning Mine coal is shown in Figure 6. Comparing results with Ireland coal, it is seen that the residue particles are finer and unlike the Ireland case, their size is relatively insensitive to extraction conditions.

The smaller particle size is one reason for the low settling rate of the Browning Mine extraction effluents. Another reason is that in contradistinction to the Ireland coal case, little or no extract comes out of solution on cooling.

The function of decane addition likely is to precipitate a portion of the extract and thus cause agglomeration of the fine residue particles to enhance their settling rate. Like the Ireland case, the precipitated extract is largely composed of benzene insolubles.

The efficiency of collection of fine particles is better for the Browning Mine coal after addition of decane than in the corresponding case for Ireland Mine coal where no decane is used. This can be seen by comparison of Figures 7 and 8. It is concluded that decane addition is very effective in causing agglomeration of fine particles.

Extensive data have not been obtained with other coals, but subbituminous coals from Montana behave similarly to the Browning Mine coal. Illinois bituminous coals show an intermediate behavior, i.e., settling may be achieved without additive, but not at as high a rate as in the Ireland coal case.

The extracts of lower rank coals appear to be lower in benzene solubles, and this may also explain the fact that extract precipitation does not occur on cooling but requires addition of a deasphalting solvent. A comparison, given below, of the residuum overflow extract for two "comparable" runs with Ireland Mine and Browning Mine coal illustrates the lower benzene insoluble content for the extract in the latter case:

Coal	Ireland Mine	Browning Mine
Condition or Run No.	Condition C	Run 45
Solvent/Coal Ratio	2	2
Extraction Depth	76	68
Overflow Residuum Extract		
Solvent Fractionation, Wt %		
Benzene Insolubles	33.2	20.1
Asphaltenes	39.4	48.5
Heavy Oil	27.3	31.4

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TABLE I

Analysis of Coal Feedstocks

Coal	Ireland Mine	Browning Mine	
		Batch A	Batch B
Proximate Analysis, MF Wt %			
Volatile Matter	42.4	41.1	40.9
Fixed Carbon	50.0	51.3	51.9
Oxidized Ash	7.6	7.6	7.2
Elemental Analysis, MF Wt %			
Hydrogen	5.36	5.05	5.03
Carbon	75.75	74.58	76.06
Nitrogen	1.44	1.39	1.31
Oxygen (difference)	6.67	10.32	10.06
Sulfur (total)	3.87	1.06	0.40
Sulfur (pyritic)	1.74	0.32	0.07
Sulfur (organic)	2.13	0.74	0.33
Wet Screen Analysis, MF Wt %			
+60 mesh	0	0	0
60 x 100 mesh	3.8	1.9	26.2
100 x 200 mesh	28.9	26.2	26.6
200 x 325 mesh	32.1	25.0	16.9
-325 mesh	35.2	46.9	30.3
Heating Value, Btu/Mf lb	13,407	--	13,402
Max. Gieseler Fluidity, DDPM at Temperature, °F	> 24,000 at 774°F	← < 1 →	

TABLE II

Analysis of Natural Solvents

Source		
Cresap Run No.	56	
	Hydro Oil	Recycle Oil
Ultimate Analysis, Wt %		
Hydrogen	9.56	9.08
Carbon	90.04	89.92
Nitrogen	0.37	0.16
Oxygen (direct)	0.24	0.60
Sulfur	0.15	0.25
TBP Distillation, Wt %		
IBP °C	180	200
IBP x 250°C	34.2	35.4
250 x 300°C	27.9	48.9
300 x 350°C	20.0	9.5
350 x 474°C	8.9	3.6
+474°C	7.7	2.0
Holdup + Loss	1.3	0.6
Gas Chromatographic Analysis, Wt %		
Light Ends	23.0	12.9
Tetralin	2.7	0.9
Unidentified	20.0	11.2
Naphthalenes	3.1	3.6
Unidentified	5.9	2.3
Methylnaphthalenes	11.9	19.2
Higher Boilers	33.4	49.9

TABLE III

Batch Extraction and Settling
Results with Ireland Mine Coal

A. Experimental Conditions

Series	A	B
Solvent	25% Hydro Oil 75% Recycle Oil	100% Hydro Oil
Solvent/MF Coal, Wt. Ratio	1.5	1.5
Extraction Temperature, °F	710	710
Extraction Residence Time, min.	60	60
Settling Temperature, °F	600	600

B. Experimental Results

Extraction Depth, % of MAF Coal	77	86
Initial Settling Rate, in/min	2.0	0.4
Properties of Extract in Clarified Layer, Wt %		
Cresol Insolubles	3.3	2.8
Total Ash	0.14	0.27
Fine Ash (-.45 μ dia.)	0.11	0.14

TABLE IV

Summary of Continuous Extraction Results

A. Conditions

Condition	A	B	C	D
Recycle Solvent Hydro Oil	3	0	3	0
Solvent/MF Coal	1.5	1.5	2	2
Slurry Feed Rate, lb/hr	30.5	13.8	30.6	28.9
Extraction Temperature, °F	750	727	740	745
Residence Time, min	24	54.8	24.1	25.2

B. Results

	A	B	C	D
Yields, Wt % MAF Coal				
Conversion	78.3	85.1	76.4	85.5
Extract + Polymer	84.9	86.3	77.0	85.0
Water	2.4	3.7	1.4	1.0
Gases + H_2S + NH_3	1.2		0.9	1.3
MAF Residue	21.7	14.9	23.6	15.6
Total	110.2	104.9	102.9	102.9
Polymerized Solvent Plus H_2 Transfer, Wt % MAF Coal	10.2	4.9	2.9	2.9

TABLE V

Effect of Extraction Conditions on Settler Performance

Extraction Condition	A	B	C(1)	D	D(2)
Solvent/MF Coal, Wt Ratio	1.5	1.5	2	2	2
Coal Conversion, Wt %	78	85	76	84	85
Settler Temperature, °F	←		600		→
Overflow Rates, $lb/hr\text{-}ft^2$	247	239	516	489	524
Wt % of Ash Out					
To Overflow	2.5	33.2	1.5	1.4	2.0
To Underflow	97.5	66.8	98.5	98.5	98.0
Extract Quality, Wt %					
Wt % Total Ash	0.22	3.30	0.16	0.16	0.21
Wt % Fine Ash (-.45 μ)	0.08	0.12	0.04	0.09	0.06
Extract Recovery in Overflow, Wt % of Feed to Settler	86.6	88.3	84.9	84.2	85.6

(1) 135% stoichiometric H_2SO_4 added.
(2) 106% stoichiometric H_2SO_4 added.

TABLE VI

Batch Extraction and Settling Results
With Browning Mine Coal
Settler Temperature = 600°F

Extraction Temperature, °F	735	737	768	737	774
Time at Temperature, min.	30	30	30	20	21
Extraction Solvent	100% Methylnaphthalene	100% Methylnaphthalene	75% MN 25% tetralin	75% Sunoco FS[1] 25% tetralin	50% MN 50% tetralin
Solvent-to-MF Coal Wt Ratio	4.0	3.8	1.5	3.0	2.08
Extraction Depth, Wt % MAF Coal	36.1	36.1	58.1	53.7	67.4
$\frac{\text{Decane}}{\text{Extraction Solvent}}$, Wt Ratio	0	0.06	0	0.105	0.251
Initial Settling Rate, in/min	0	0.22	0.10	0.25	> 1.4

(1) Petroleum derived solvent mainly consisting of mixed methyl- and dimethyl naphthalenes.

TABLE VII

Continuous Extraction and Settling
Results with Browning Mine Coal
Extraction Solvent/MF Coal = 2.08
Feed Solvent = 49.4% tetralin-50.4% methylnaphthalene
Settler Temperature = 600°F
Extraction Temperature = 775°F

Run No.	45-1	45-2	45-3	45-4	45-5
Slurry Feed Rate, lb/hr	14.7	15.0	15.1	14.9	13.8
Residence Time, min	42.6	41.3	40.9	41.2	43.5
Yields, Wt % MAF Coal					
Conversion	69.6	66.8	68.2	69.4	67.4
Extract	58.5	51.9	52.8	55.0	60.5
Decane/Extraction Solvent, Wt Ratio	0.104	0.133	0.200	0.252	0.309
Overflow Rate, $lb/hr\text{-}ft^2$	286	282	303	286	304
Settler Upflow Velocity, in/min	1.12	1.16	1.29	1.28	1.35
Wt % of Ash Fed to Settler in Overflow	30.7	14.0	5.9	1.1	0.8
Product Extract Ash Content, Wt %	4.05	2.35	0.95	0.24	0.12

TABLE VIII

Terminal Velocities of Extraction Residue Particles

Condition	A	B	C	D
Solvent/Coal Ratio	1.5	1.5	2	2
Conversion	78	85	76	85
Median[1] Particle Size, μ	20	12	28	16
Terminal Velocity, in/min	0.42	0.15	0.82	0.27
75%[2] Particle Size, μ	54	22	70	34
Terminal Velocity, in/min	3.1	0.51	5.1	1.2
Initial Settling Velocity of Slurry	2.0	0.4	--	--

(1) 50% of particles smaller than size given.
(2) 75% of particles smaller than size given.

Figure 1
Hydrogen Donor Extraction Unit With Settler

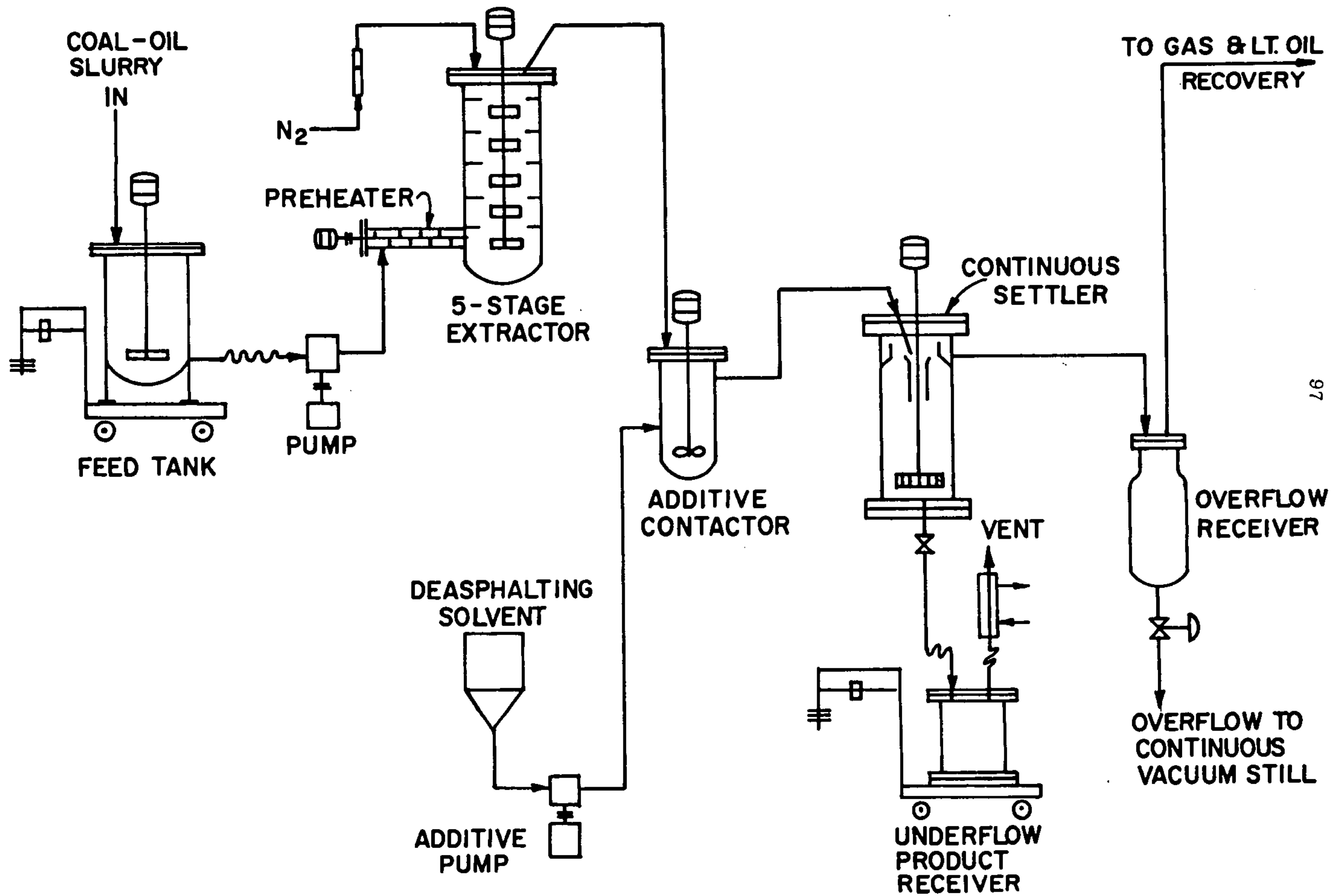


Figure 2
Ash Breakthrough To Settler Overflow
1-1/2:1 S/C Ratio 70-80% Conversion Condition A

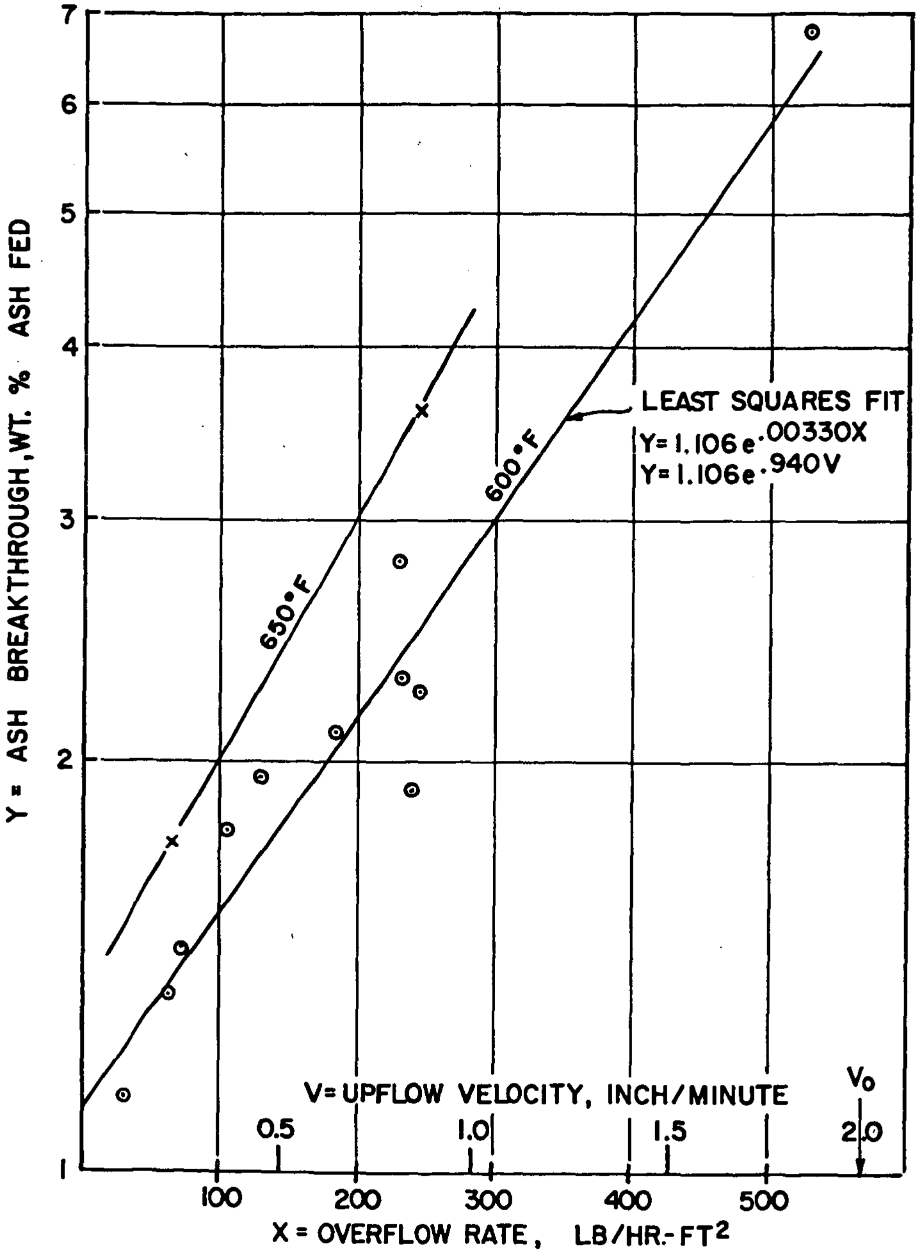


Figure 3

Relation Between Coal Conversion & Hydrogen Transfer Browning Mine Coal

Point	Run 197.01	% Tetralin In Solvent	Temperature	Residence Time (Min.)	S/C Ratio	Coal Batch
1	41	0	749 °F	24.1	4	A
2	35	50	713	20.9	1.5	A
3	44	28.9	746	23.5	3	A
4	40	50	754	26.8	1.5	A
5	34	50	749	42.4	1.5	A
6	46	50	770	42.6	2	A
7	51	50	772	43.4	2	B
8	36	50	774	41.5	1.5	A

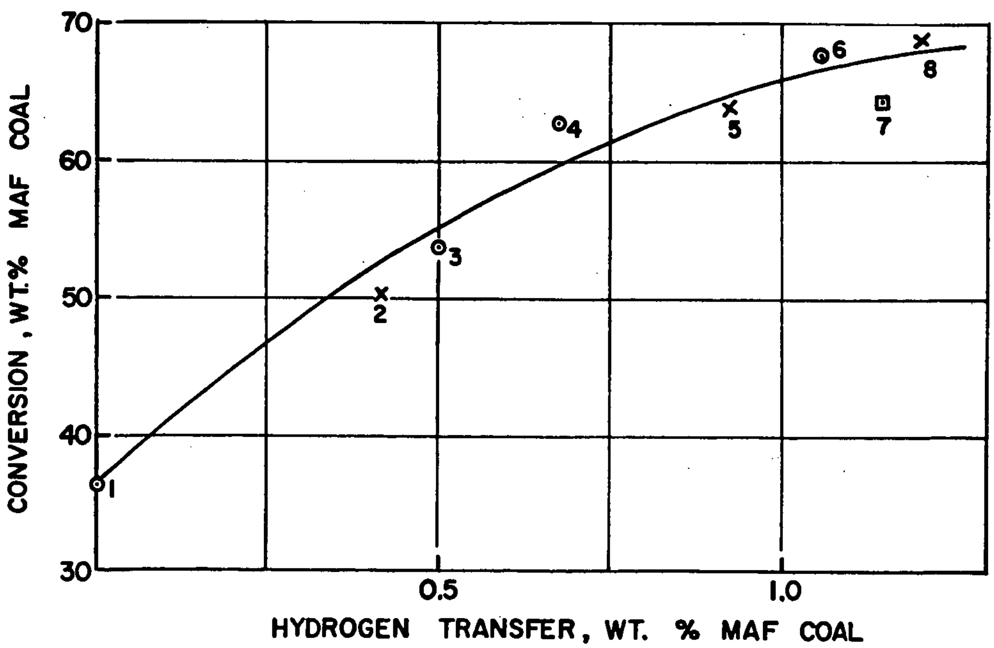


Figure 4

Comparison Of Observed And Predicted Hydrogen Transfer From Continuous Extraction Runs With Browning Mine Coal

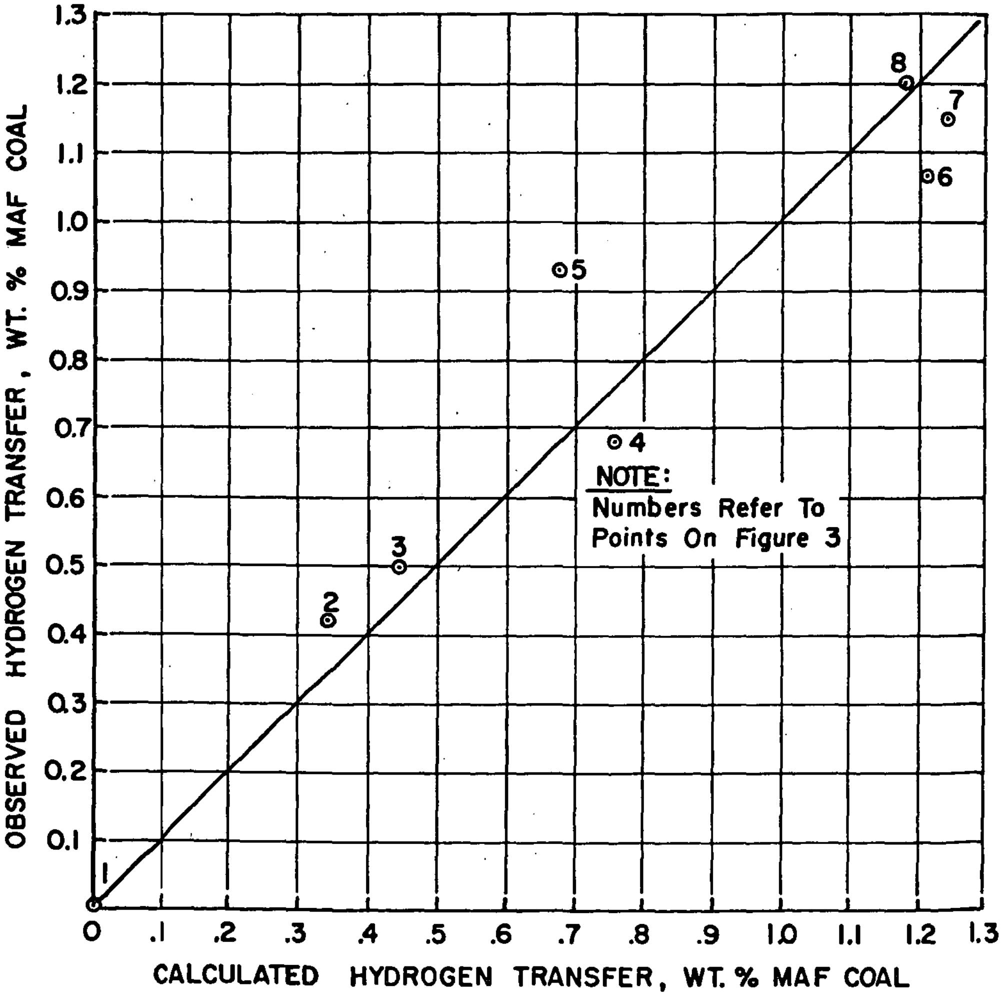


Figure 5

Effect Of Temperature And Decane Proporation On Settler Separation Efficiency

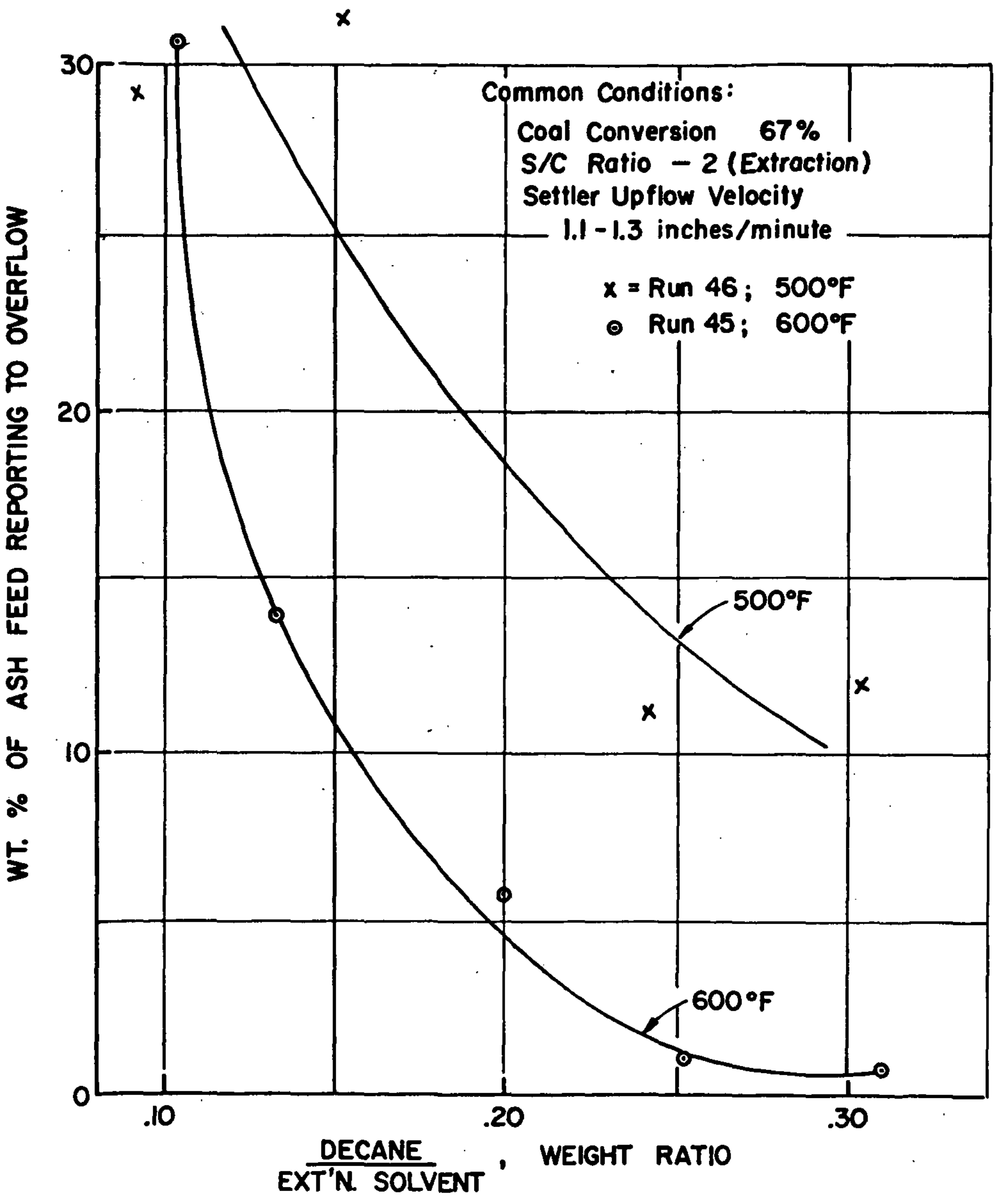


Figure 6

Particle Size Of Insolubles

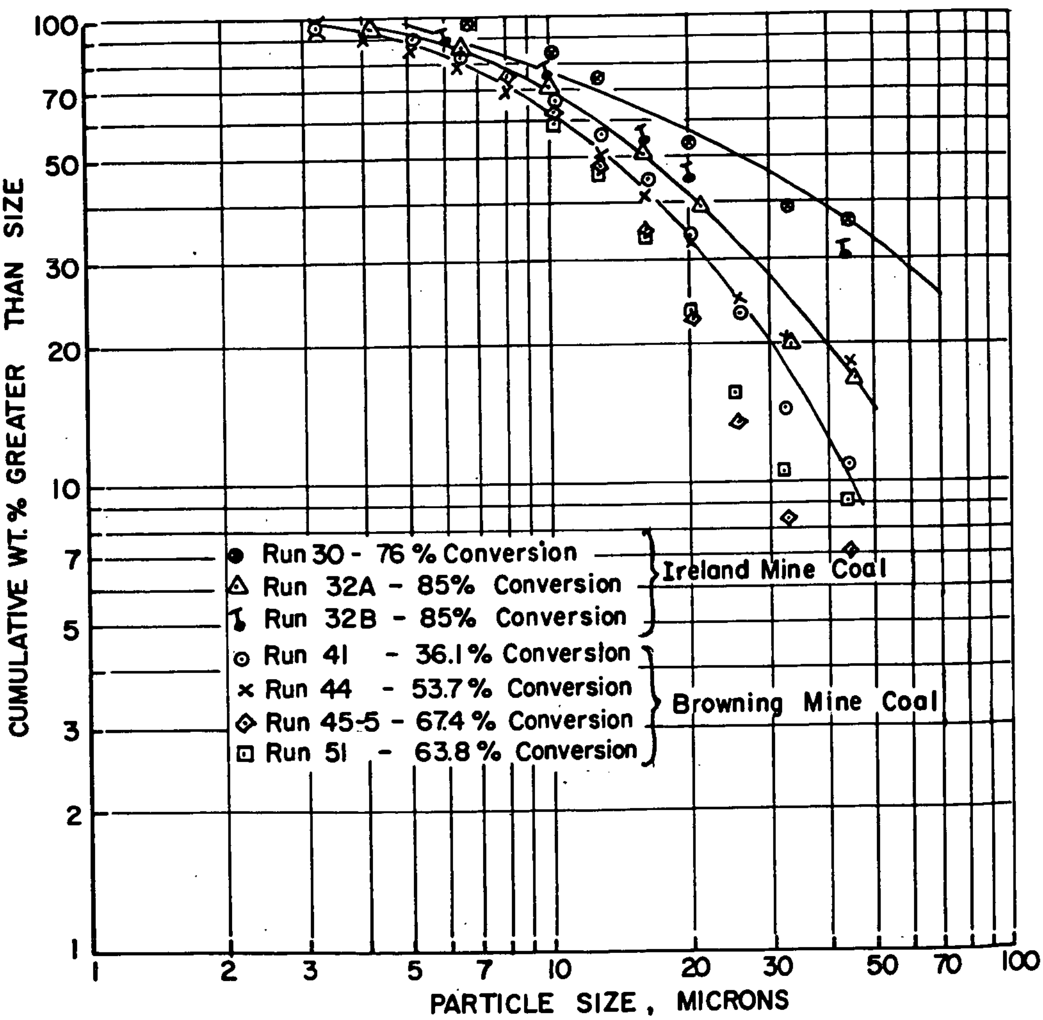


Figure 7

Fractional Removal Efficiencies Of Residue Particles
Ireland Mine Coal - Solvent/Coal Ratio = 1:5

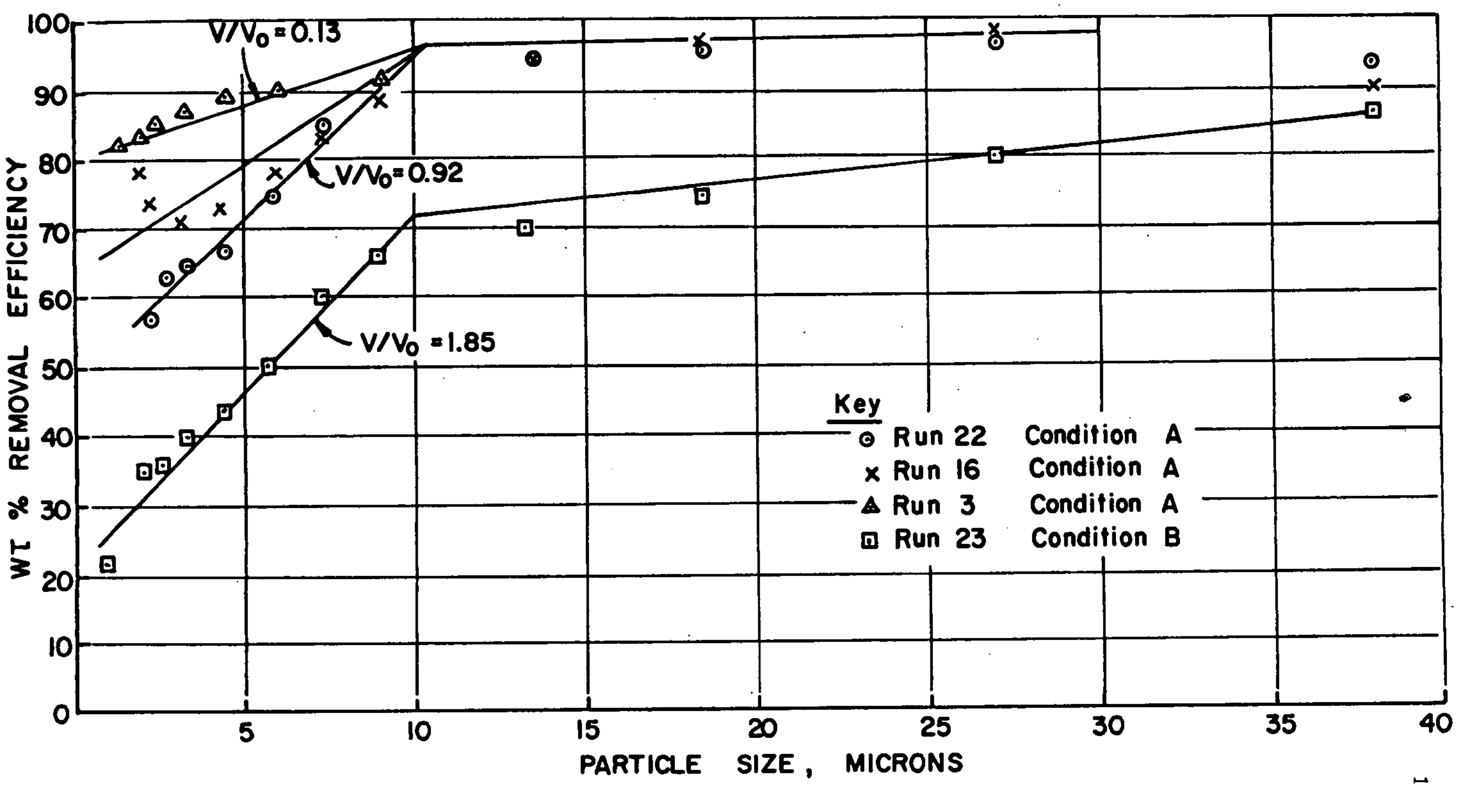
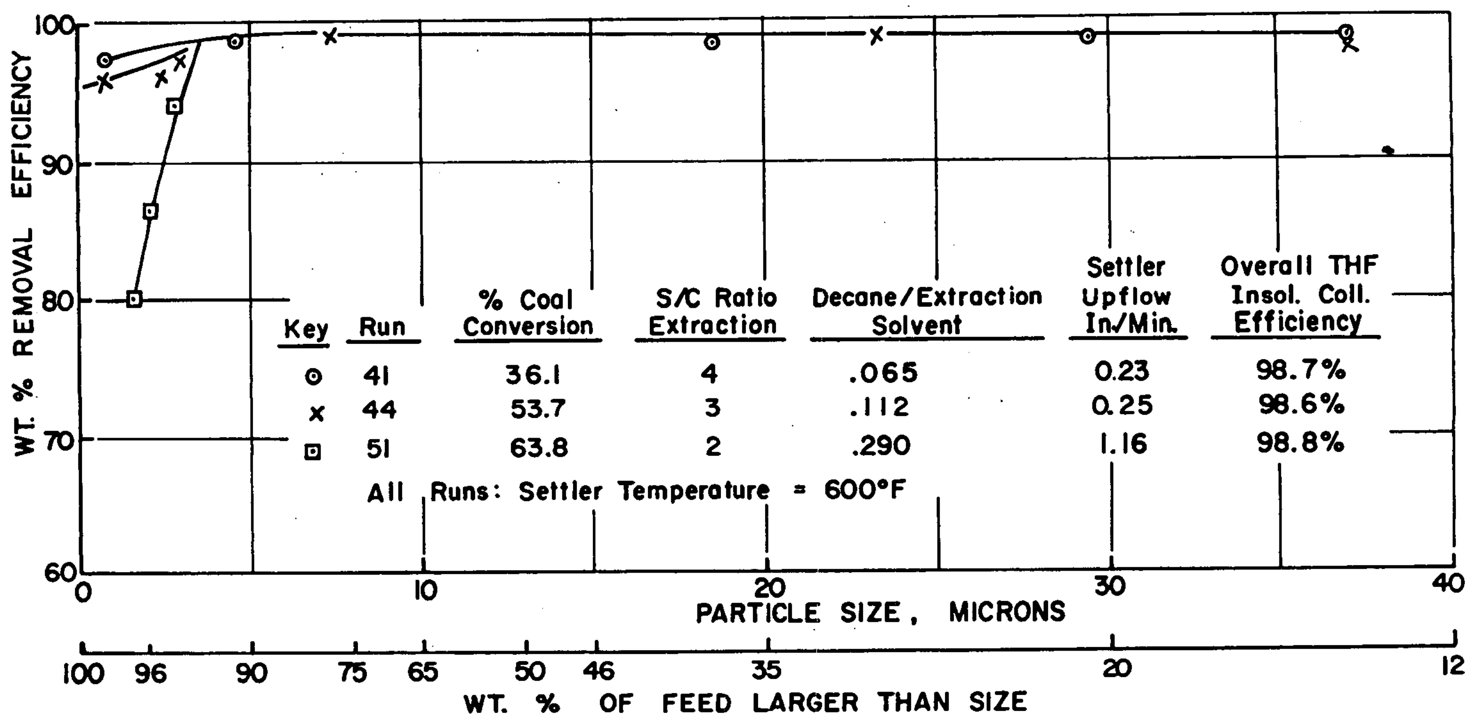


Figure 8

Fractional Removal Efficiencies Of THF Insoluble Extraction Residue Runs 41, 44 and 51



DEASHING OF COAL LIQUEFACTION PRODUCTS VIA PARTIAL DEASPHALTING. II - HYDROGENATION AND HYDROEXTRACTION EFFLUENTS

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INTRODUCTION

A previous paper described the deashing of extraction effluents produced by hydrogen-donor extraction of bituminous and subbituminous coals.(1) The method described was the use of batch and continuous gravity settling with and without the use of deasphalting solvents to accelerate the settling process.

The present paper presents data on the extension of the same deashing technique to coal liquefaction products produced by direct hydrogenation of Illinois No. 6 bituminous coal. Deashing experiments were conducted both with products produced by liquid-phase hydrogenation in the presence of an ebullated bed of hydrofining type catalyst (H-Coal Process)(2) and with products produced by hydroextraction, i.e., without added catalyst (PAMCO Process).(3)

In contrast with the previous donor extraction case, the addition of a deasphalting solvent was required in both the H-Coal and hydroextraction cases to achieve an acceptable rate of deashing.

The hydroextraction products were produced in the CCDC bench-scale unit. Data are presented with respect to solvent balance, product yields and properties in hydroextraction as well as the deashing behavior of the hydroextraction effluents. Continuous unit data are presented in detail for the hydroextraction work while the batch work is briefly summarized.

Data are presented for deashing of H-Coal bottoms in both batch and continuous units.

EXPERIMENTAL

H-Coal Bottoms - Materials and Procedure

The basic material for the deashing studies was the vacuum bottoms from processing of Illinois No. 6 coal via the H-Coal Process. The material was produced by Hydrocarbon Research, Inc. for the Office of Coal Research in their 8" I.D. Process Development Unit. The detailed conditions for production of this material are given in Table 15 of Reference (2). Operating conditions were varied somewhat during this run. The average operating conditions were 2700 psig, 30 lbs coal fed/hr-ft^3, 825°F and an average catalyst age of 230 hours.

The material "as received" consisted of the vacuum distillation residue from the H-Coal hydro bottoms. The material accordingly had most of the -975°F distillate oils removed. The analysis of the material is given in Table I.

The deashing in practice likely would be done prior to removal of the distillate oils. The material was accordingly reconstituted to simulate its original form by solution at 600°F in natural recycle solvent from Cresap, W. Va. A ratio of 1.25 parts solvent to 1 part of vacuum bottoms was used for both batch and continuous runs.

The origin and analyses of the Cresap recycle solvent were given previously.(1) n-Decane (Phillip's Technical Grade Minimum Purity 95%) was used exclusively as the deashing solvent in this work.

The batch settling experiments were carried out in the same manner as previously described for coal extraction products. The "reconstituted" slurry was heated with stirring to 720°F, n-decane was then added in prescribed amount and the mixture cooled to 600°F. The agitation was stopped and the slurry allowed to settle. Both settling rates and clarity of the upper phase after about three hours of settling were determined.

The same continuous unit[1] used for extraction and deashing of extraction effluent was used for deashing of the "reconstituted" H-coal bottoms. The extractor in this case served to preheat the slurry to 720°F. n-Decane was introduced into the middle stage of the extractor. The outlet slurry was cooled to 600°F before entering the settler which was also operated at 600°F. Only one continuous run was made due to limitations in supply of material.

The unit was started with solvent flow through all vessels until proper temperature conditions were established. The H-Coal slurry was then passed through the unit for a line-out period of nine hours to displace the start-up solvent. A material balance ensued for a period of four hours during which time samples of all appropriate streams were taken for analyses.

Hydroextraction - Materials and Procedure

The hydroextraction work was carried out with an Illinois No. 6 bituminous coal from the Burning Star Mine of Consolidation Coal Co. Analysis of the coal as fed to the hydroextraction unit is given in Table I.

A batch program was carried out prior to the continuous work in the same one-gallon autoclave previously used for donor extraction.[1] Anthracene oil was used as solvent and n-decane as deashing solvent. The experimental procedure was very similar to that previously described.[1] The autoclave was heated to 825-850°F with pure H_2 flowing slowly through the autoclave maintained at 1000 psig. The hydrogen flow was then stopped, n-decane added, and the reactor cooled to 600°F. The agitation was stopped for measurement of the settling rate.

Continuous hydroextraction runs were carried at two operating pressures of 950 psig and 2000 psig, respectively.

Operation at 950 psig

The 950 psig runs were conducted with essentially the same equipment as used previously in the donor extraction work.[1] Revisions were made, however, to accommodate the use of hydrogen as shown in the schematic flow diagram of Figure 1. Facilities were added for feeding a metered stream of pure hydrogen. The hydrogen was preheated and added to the feed slurry just before the latter entered the horizontal stirred preheater.

Another substantial change was the introduction of a primary receiver or "hot separator" between the extractor and the additive contactor. This served to disengage the gas and volatilized solvent from the product slurry. The primary receiver was normally operated at 650°F.

The operation of the hot separator resulted in a removal of a considerable fraction of the product slurry as vapor. The experimental results shown in Table II give the actual liquid feed rate to the settler as a weight fraction of slurry feed to the hydroextraction unit.

The liquid level in the separator was maintained by operation of a tungsten carbide-trimmed, let-down valve actuated by a liquid level controller. The final product was similarly handled in the overflow receiver where the product was let down to the pot of a vacuum still.

A series of runs was first conducted while bypassing the settler to survey the effect of the variables.

The start-up solvent was a coal-tar derived anthracene oil obtained from Allied Chemical Co. The oil was stabilized before use by running it through the unit with hydrogen at 950 psig, but without coal added, for six cycles. Polymer formed was removed by fractionation in the vacuum still. The still was operated in a semi-continuous fashion. Before the contents of the pot were removed, feed to the still was interrupted, the vacuum was reduced to 1 mm Hg while the temperature of the stirred liquid in the pot was maintained at 240°C until no more vacuum distillate was collected. The composition of the "stabilized" anthracene oil is given in Table II.

The second series of runs was conducted with the settler operating and n-decane added to increase settling rate.

A final series of runs was conducted in an attempt to generate natural solvent. To minimize physical solvent losses, the operation of the settler was bypassed. The total hydroextraction effluent was processed through the vacuum still to recover all distillates. The overhead distillate was then fractionated in a continuous atmospheric fractionating column packed with Goodloe packing, and having the equivalent of about 50 theoretical plates. The light cut boiling below 240°C at 1 atm was removed in this way before recycle of the solvent to the extraction unit.

Two types of operation were conducted in the above recycle solvent program. The initial method consisted of direct recycle of spent solvent to the hydroextraction unit. The second operation consisted of a "hybrid" type operation where either one-half or all of the recovered solvent was rehydrogenated over a fixed-bed, nickel molybdate catalyst before recycle to the hydroextraction unit. The final operation returned to direct recycle. Results of the final recycle operation only are reported here.

The hydroextraction was normally operated with a stirrer speed of 600 rpm. The system was inoperable due to coke formation when the stirrer speed was reduced to 300 rpm.

<u>Operation at 2000 psig</u>

The 2000 psig operations were conducted in a similar manner. A new five-stage, stirred extractor was build for the higher pressure with overall dimensions of (preheater and extractor) of 5.2" I.D. by 49.8" in height.

The initial operations at 2000 psig were conducted in two phases without operation of the settler. The first phase consisted of a short study of the system variables using the anthracene oil stabilized at 2000 psig. The second phase consisted of operation at constant operating conditions to generate natural solvent.

The natural solvent was then used in a final campaign in which both the continuous extraction and settler units were operated simultaneously. In this campaign the overflow and underflow streams were mixed and sent to the vacuum still for recovery of solvent. n-Decane was again used exclusively as the deashing solvent in this work.

The vacuum still during the 2000 psig hydroextraction campaign was operated to a final pot temperature of 290°C at 1 mm Hg, as contrasted to the final pot temperature of 240°C at 1 mm Hg used in the 950 psig campaign. The corresponding atmospheric boiling points are 474°C and 535°C, respectively. It should be recognized, of course, that some lower-boiling materials will be retained in the pot liquids by virtue of dilution with higher-boiling residue.

<u>Analytical and Calculational Procedure</u>

The analytical procedures were for the most part identical to those reported earlier.[1] Some slight differences are noted, however. Boiling tetrahydrofuran was used in the H-Coal work instead of cresol (in all other work) to characterize the quantity of insoluble residue. Results of the two solvents are, however, very similar. Slightly-higher insolubles are obtained with tetrahydrofuran.

The characterization of the solvents by boiling point in this work was determined by retention time in gas chromatography. A Perkin-Elmer 900 gas chromatograph was used. The column used was of an open tubular type, 100' x 0.0465" I.D., support coated with an Apiezon L substrate containing a finely divided siliceous support in the coating solution. The column retention times were calibrated with known compounds of the type present in the coal derived solvent such as tetralin, naphthalene, methylnaphthalenes, phenanthrene, pyrene and chrysene.

Coal conversion in the hydroextraction runs was defined on the same basis as in the previous donor extraction case.[1]

The hydrogen consumption was measured in two ways, by direct measurement of hydrogen gas in and out excluding flash gases and by forced elemental balance. The latter generally was higher than the former as might be expected due to small leaks, etc. Accordingly, only the latter values are reported.

The yield structure and material balance were arrived at by the following procedure:

a. Force H_2S, NH_3 and H_2O yields by forced N, O and S balances.
b. Force total material balance, i.e., solvent plus coal plus H_2 consumed = products ex H_2 gas.
c. Iterate steps a) and b) until a simultaneous solution is obtained.

The material balance invariably was quite good such that very little forcing under step b) was required.

EXPERIMENTAL RESULTS

H-Coal Bottoms

A summary of the batch deashing runs is given in Table III. The initial settling rate for the 500 and 600°F runs are plotted in Figure 2 versus decane/slurry weight ratio. It is noted that the settling rates are nearly identical at both temperatures. When the decane/slurry ratio was increased to 0.35, the settling rate was too fast for accurate measurement. Only a minimum rate can be specified as shown in Table III.

The "equilibrium" clarity of the upper phase is plotted against the decane/slurry ratio in Figure 3. It is noted that a much lower ash "ultimate" product can be achieved at 500°F. Wall deposits were noted, however, in some of the 500°F runs which raised some doubt about operability of a continuous settler operated at this temperature.

For this reason, the continuous demonstration run was carried out at 600°F. Conditions and results of this run are given in Table IV.

The results of the continuous and batch runs are in good agreement. The settler upflow velocity of 0.37 in/min (Table IV) is equivalent to an initial settling velocity in the batch unit at a slightly lower decane/slurry ratio of 0.20 (Table III). The ash content of 0.13 wt % is equivalent to the equilibrium clarity of the batch run of 0.18 wt %.

The amount of precipitated residuum was calculated by the method outlined in a previous paper.[1] The value obtained, i.e., 7.9 wt % of the +474°C feed, is also in the same range indicated by the batch measurements.

Recovery of "soluble" residuum in the overflow was 76.5%. This value could be improved, of course, by back washing of the underflow.

Hydroextraction

The initial batch experiments on hydroextraction were made with anthracene oil solvent at 1000 psig, 825°F extraction temperature and 600°F settling temperatures. The settling rate was substantially zero without addition of deasphalting solvent. A relatively high settling rate of 1.9 in/min was obtained, however, by addition of decane in a weight ratio of 0.3 to extraction solvent.

The initial operations in the continuous unit utilized stabilized anthracene oil as the solvent at 950 psig total pressure. A survey of the temperature variable was made at constant slurry feed rate of 30 lb/hr and constant total pressure of 950 psig. The hydrogen partial pressure at the extractor exit was in the range of 800-830 psia. The optimum temperature at this pressure was 800°F, giving a conversion of 82%, as results in Table V indicate. A temperature of 825°F was chosen for more intensive study, however, since the residuum extract showed a more favorable lower sulfur content, i.e., 0.86% S versus 1.00% S at 800°F, as noted in Table V.

It was therefore decided to generate natural solvent from coal by continuous recovery and recycle of solvent at 825°F and to simultaneously study the deashing and extraction during the production of the natural solvent.

The deashing via continuous settling with decane addition was studied early in the solvent recycle program. A typical result is shown in Table VI where good deashing was obtained at a decane-to-extraction solvent ratio of 0.29 and a settler upflow velocity of 1 in/min. This result is roughly in agreement with batch results cited above where under comparable conditions the initial settling velocity was 1.7 in/min.

The solvent recycle program was finally abandoned after it was found that the low pressure operation could not be self-sustained without periodic addition of fresh anthracene oil.

The failure to close solvent balance is clear from the product yields cited in Table V. The data at 825°F and 950 psig represent average performance after about 25 cycles. It is noted that there is a net deficiency of 5.2% of recycle solvent in the boiling range used, i.e., 240 x 474°C. The use of a higher endpoint, as noted, in Table V would have substantially reduced the solvent deficit but would not have eliminated it. At any rate, handling losses were sufficiently high such that it would have been impossible to generate pure natural solvent even with the higher distillation endpoint. Accordingly, no further deashing studies were carried out at the low pressure level.

It is apparent, however, from the data given in Table II, that significant even though partial displacement of the initial solvent was obtained in the 950 psig operation. This is illustrated by the lower boiling range and higher hydrogen content after 25 cycles as compared with the stabilized anthracene oil.

The hydroextraction operation was then carried out at a higher total pressure, i.e., 2000 psig, with a hydrogen partial pressure approximately 1850 psia. A solvent surplus was readily generated at 2000 psig, partly because of the higher pressure and partly because of the higher distillation endpoint used in recovery of recycle solvent.

Steady operation was sustained for a total of 500 hours until the initial solvent was largely displaced. The product and yield distribution after generation of natural solvent is given in Table V. The principal differences as compared with the 950 psig operation, i.e., higher coal conversion, positive net solvent generation, higher overall distillate yield and lower extract sulfur content, are clear from the data presented in Table V. The apparent reduction in extract sulfur is not very great, i.e., 0.86 to 0.7. The actual reduction likely is considerably greater. The sulfur content of the 950 psig residuum is artificially low since it contains a significant quantity of 474 x 535°C solvent polymer and heavy oil not present in the 2000 psig product.

The continuous deashing of the 2000 psig product with n-decane additive was then studied with the results shown in Table VI. It is again shown that very little ash removal is obtained without addition of decane. Almost complete deashing is achieved by use of a ratio of decane-to-extraction solvent of 0.50. At this condition, it was determined by the method outlined previously,[1] that the deashing was accompanied by precipitation of 16 wt. % of the cresol-soluble residuum fed to the settler.

DISCUSSION OF RESULTS

The particle size distribution of the cresol insolubles in the H-Coal bottoms hydroextraction at 2000 and 950 psig are compared in Figure 4. It is noted, i.e., the size of the residue decreases with increasing severity of hydrogenation in going from 950 to 2000 psig hydroextraction to 2700 psig catalytic hydrogenation (H-Coal). All of the products show a finer size residue than the donor extraction products discussed in the earlier paper.[1]

The relative ease of deashing might be expected to follow the same sequence as residue size. The results in Table VI are in agreement with this in that a higher decane-to-extraction solvent ratio is required to deash the 2000 psig as compared with the 950 psig hydroextraction product. Unfortunately, no valid comparison can be made between the H-Coal and the hydroextraction products because of the fact that the latter was artificially "reconstituted" by use of Cresap recycle solvent.

The mechanism of deashing as discussed previously, undoubtedly involves agglomeration of fine residue particles by precipitation of heavy asphalt.

The data in Table VII clearly show that the benzene-insoluble content follows the same trend as residue size with increasing severity of hydrogenation treatment. Thus, from this point of view also, a larger quantity of deasphalting solvent would be required to achieve an equivalent amount of benzene-insoluble rejection. Unfortunately, insufficient data are available to verify this supposition.

The failure to close the solvent balance in hydroextraction at 950 psig is consistent with results published previously.[8] The successful generation of natural solvent at 2000 psig is consistent with recent results on the PAMCO process published by Anderson.[9]

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TABLE I

Analysis of Feed Materials

	Illinois No. 6 Coal Burning Star Mine	H-Coal Vacuum Bottoms
Proximate Analysis		
Moisture and Distillate (-474°C) Free, Wt %		
Volatile Matter	41.4	--
Fixed Carbon	48.4	--
Ash Oxidized	10.2	24.3
Ultimate Analysis		
Moisture and Distillate (-474°C) Free, Wt %		
Hydrogen	4.71	5.01
Carbon	70.79	66.63
Nitrogen	1.27	1.20
Oxygen (diff.)	10.14	0.92
Total Sulfur	2.93	1.98
Organic Sulfur	2.15	1.45
Pyritic Sulfur	0.54	--
Sulfate Sulfur	0.24	--
Distillation, Wt %		
Distillates (-474°C)	0	6.3
Residue (+474°C)	100	93.7
Solvent Fractionation, wt %		
THF Insoluble	--	38.0
Benzene Insoluble-THF Soluble	--	7.0
Asphaltenes	--	29.0
Oils	--	26.0

Screen Analysis, Tyler Mesh	Wt %	Particle Size Analysis, THF Insolubles	Wt %
+28	0.1	+26 microns	1.8
28 x 48	1.6	20.7 x 26	3.3
48 x 100	18.0	13 x 20.7	13.2
100 x 200	22.4	6.5 x 13.0	34.0
200 x 325	19.5	4.1 x 6.5	35.7
-325	38.4	-4.1	12.0

TABLE II

Analysis of Feed and Product Recycle Solvents

	Solvent		
	Stabilized Anthracene Oil	After 25 Cycles, at 950 psig	Natural Solvent After 2000 psig Operation
Boiling Range by G.C., Wt. %			
-218°C	0.57	1.12	5.03
218 x 240°C	2.29	5.24	15.33
241 x 260°C	6.91	15.32	18.92
261 x 294°C	28.13	27.98	21.81
295 x 340°C	36.92	33.42	24.09
+340°C	25.18	16.92	14.82
Ultimate Analysis, Wt. %			
Hydrogen	5.92	7.48	7.84
Carbon	91.42	90.49	88.43
Nitrogen	0.94	0.36	0.67
Oxygen	1.28	1.52	2.71
Sulfur	0.44	0.15	0.35

TABLE III

Summary of Batch Settling Runs with H-Coal Bottoms

Run Number	1	6	3	5	7	4
Temperature, °F	500	→	←	600	→	→
Additive	None	n-Decane	→	→	→	→
Additive/Reconstituted Slurry, Wt Ratio	0.0	0.10	0.35	0.10	0.20	0.36
Cresap Recycle Solvent, Wt Ratio H-Coal Vacuum Bottoms	2.04	1.25	→	→	→	→
Initial Settling Rate, in/min	0.04	0.12	>> 1.1	0.12	0.38	> 1.71
Wt % Ash in Ultimate Clarified Layer	0.48	0.12	0.02	0.23	0.18	0.11
Precipitated Residuum Solubles, Wt % of Residuum Fed	(1)	(1)	(1)	(1)	(1)	7.9(2)

(1) Consistent values by solvent balance could not be obtained.
(2) Determined by filtration.

TABLE IV

Conditions and Results of Continuous Deashing Run with H-Coal Bottoms

Feed Slurry	1.25 lb Cresap Recycle Solvent / lb H-Coal Vacuum Bottoms
A. Temperatures, °F	
Pumping	600
Preheat	720
Settler	600
B. Feed and Product Rates	
Raw Slurry, lb/hr	31.3
Decane Feed, Wt % of Slurry	25
Calculated Settler Upflow Velocity, in/min	0.37
Product Split, Wt %	
Overflow	66.1
Underflow	28.7
Vents - Condensed Vapor	5.7
C. Product Quality	
Ash in Overflow, Wt %	
in Total	0.034
in +474 C Residuum	0.13
THF Insolubles in Underflow, Wt %	
Total Underflow	46.8
in +474°C Residuum	71.9
D. Calculated Wt % Residuum in Feed Precipitated	7.9
E. Wt % Recovery, THF Soluble Residuum in Overflow	76.5

TABLE V

Yields and Solvent Balance in Hydroextraction

A. Conditions			
Total Pressure, psig	950	950	2000
Extraction Temperature, °F	800	825	822
Solvent/MF Coal, Wt Ratio	2.5	2.5	2.0
Slurry Feed Rate, lb/hr	30	30	28.1
Coal Throughput, lb MF/hr-ft^3	38	38	41
H_2 Rate, SCF/lb MAF Coal	27.8	27.8	26.3
H_2 Partial Pressure at Exit, psia	~ 830	~ 800	~ 1850
Solvent Age, Cycles	15	avg. 17	Natural
B. Results			
Coal Conversion, Wt % of MAF Coal Fed	82.4	77.8	94.3
Yields, Wt % of MAF Coal			
MAF Cresol Insolubles	17.6	22.2	5.7
Extract (+474°C Residuum Solubles)	66.6	62.4	--
Extract (+535°C " ")	--	57.8	56.2
Water	6.6	6.4	9.1
$H_2S + NH_3$	2.5	2.2	2.3
$CO_2 + CO$	1.3	1.6	1.6
C_1-C_5 Hydrocarbons	4.7	5.0	7.4
C_6 x 240°C Light Distillate	4.1	6.8	6.6
240 x 474°C Recycle Solvent	-1.9	-5.2	--
240 x 535°C " "	--	-0.6	14.0
Total	101.5	101.4	102.9
H_2 Consumed, Wt % MAF Coal	1.5	1.4	2.9
Extract Sulfur, Wt %			
+474°C Residuum	1.00	0.86	--
+535°C "	--	--	0.7

TABLE VI

Results of Deashing Hydroextraction Effluent

Extraction					
Solvent/MF Coal, Wt Ratio	2.5	2.0	2.0	2.0	2.0
Solvent Age, Cycles	~ 3	Natural →	→	→	→
Temperature, °F	825	822 →	→	→	→
Pressure, psig	950	2000 →	→	→	→
Conditioning					
Temperature, °F	599	600 →	→	→	→
n-Decane/Extraction Solvent, Wt Ratio	0.29	0.00	0.31	0.49	0.50
Settling					
Temperature, °F	611	600 →	→	→	→
Free Cross Section, ft^2	.079 →	→	→	→	→
Settler Feed as Wt Fraction of Slurry Fed to Extractor	--	0.75	0.77	0.63	0.70
Overflow, $lb/hr\text{-}ft^2$	282	285	368	343	414
Overflow Velocity, in/min	1.0	0.9	1.6	1.7	1.8
Underflow, Wt % of Settler Feed	25.3	22.8	17.0	18.9	7.5
Results					
Quality of Residuum in Overflow, Wt %					
Cresol Insolubles	8.6	17.1	14.7	0.25	0.14
Ash	0.40	11.3	9.9	0.17	0.10
Sulfur	0.80	1.3	1.2	0.65	0.76
Extract Recovery in Overflow, Wt % of Extract Fed	70.1	81.1	75.0	69.0	80.4
Wt. % of Ash Fed in Settler Overflow	1.6	54.7	43.8	0.6	0.4

TABLE VII

Solvent Fractionation Analyses
- Cresol-Soluble Residue

Process	Hydroextraction		H-Coal Bottoms
Operating Pressure, psig	950	2000	2700
Operating Temperature, °F	825	825	825
Benzene Insolubles, Wt %	31.8	17.8	11.3
Asphaltenes, Wt %	40.2	60.2	46.8
Oil (+474°C), Wt %	28.0	--	41.9
Oil (+535°C), Wt %	--	22.0	--

Figure 1
Hydroextraction Unit With Settler

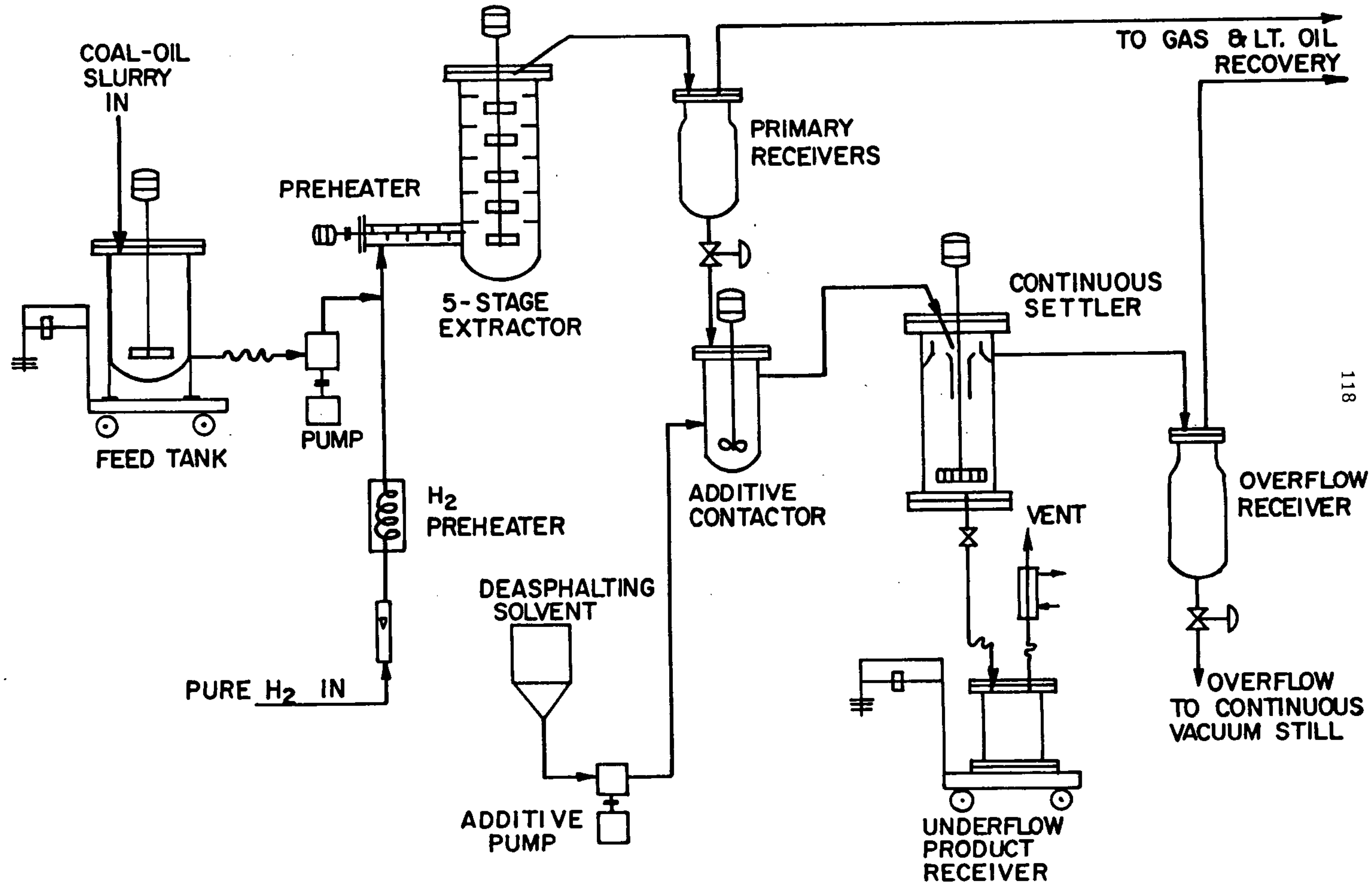


Figure 2

Settling Rate of H-Coal Bottoms Slurry
(Effect of Decane Addition)

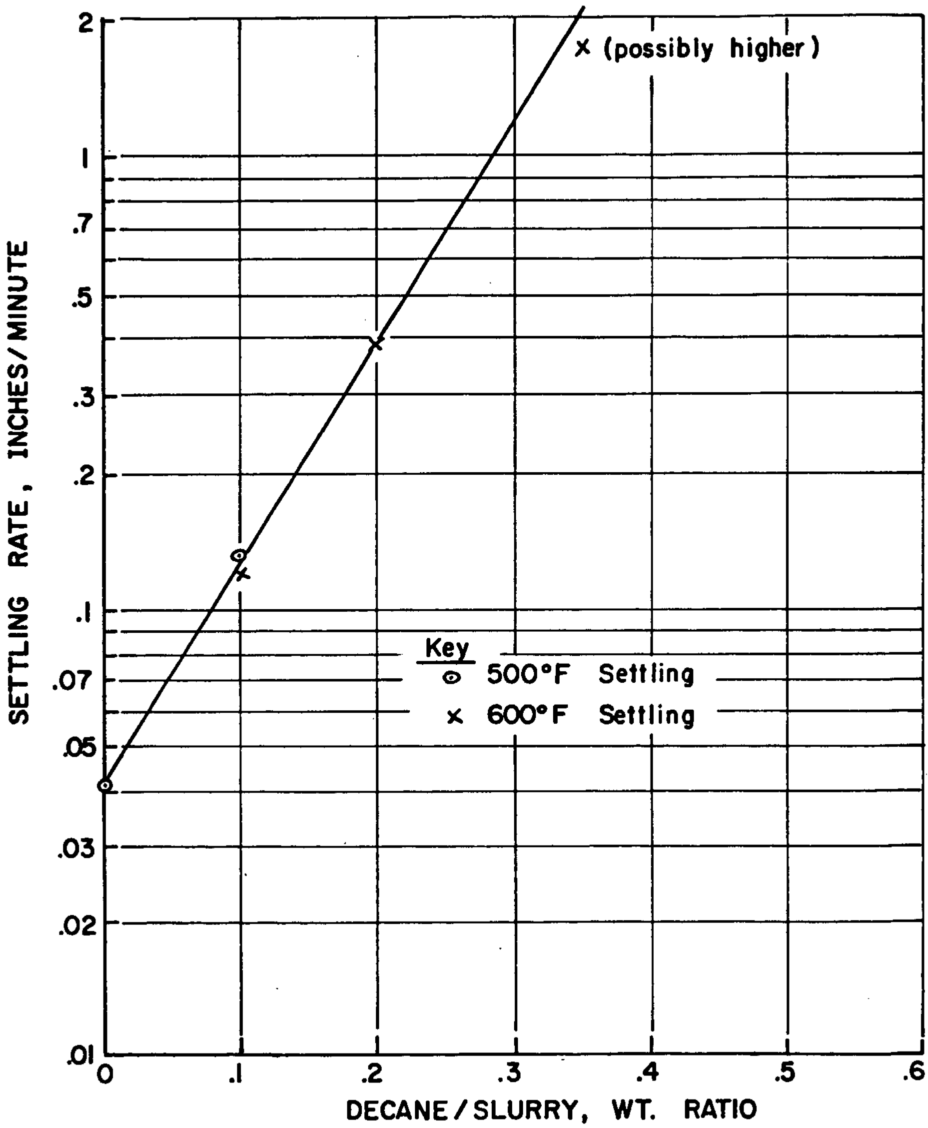


Figure 3

"Equilibrium" Clarity of Products as a Function of Decane Addition and Temperature

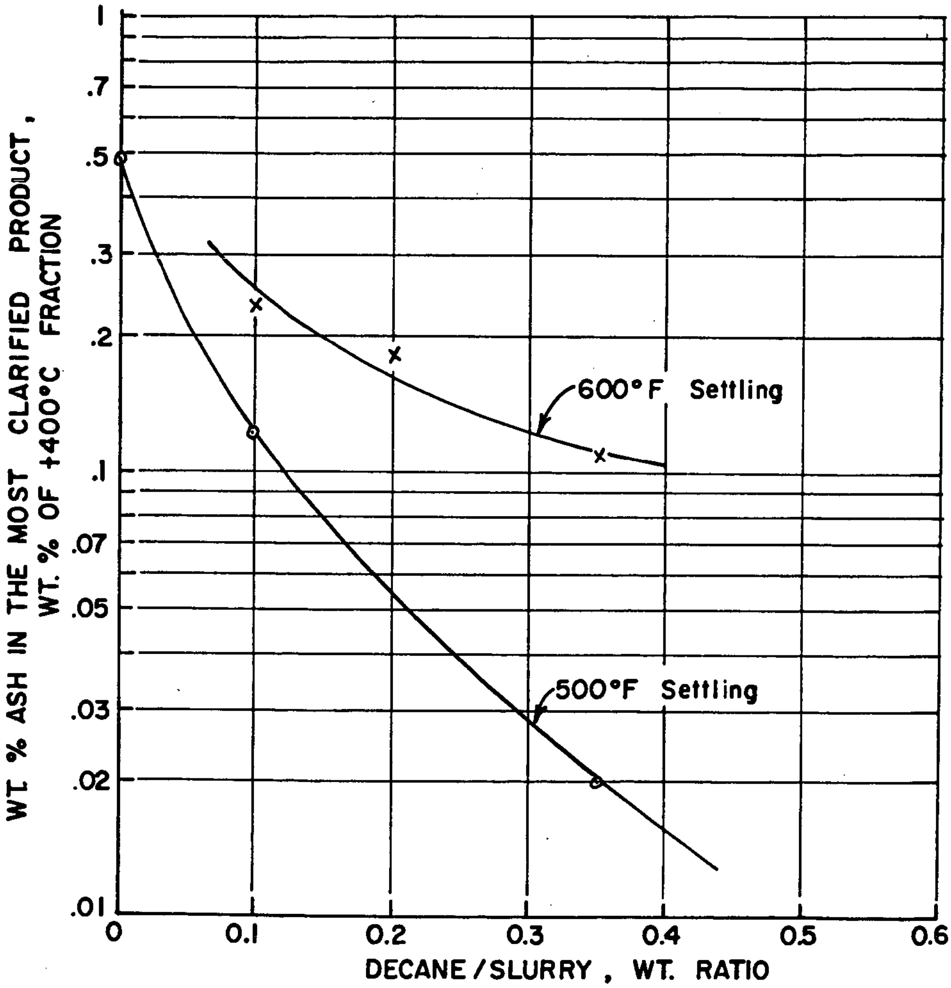
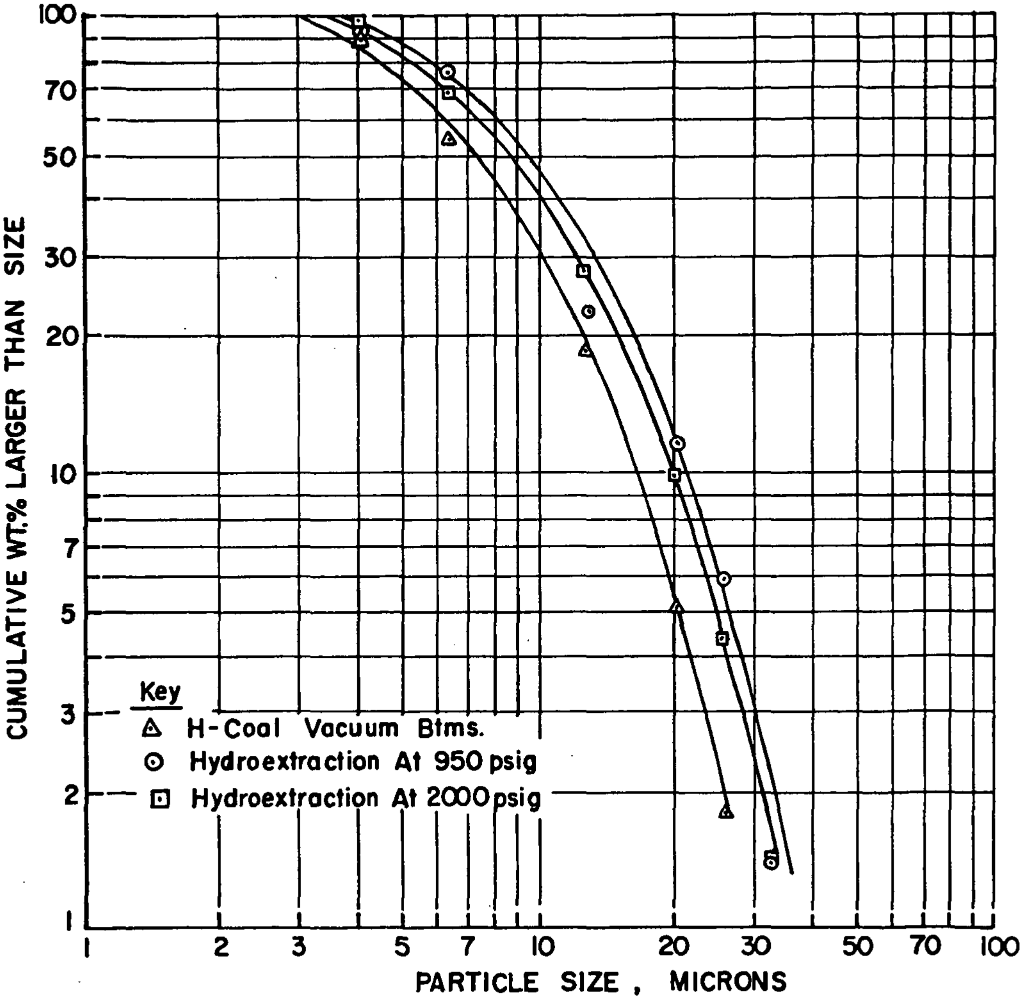


Figure 4
Particle Size of Cresol Insolubles



BATCH AUTOCLAVE HYDROGENATION OF SOLVENT REFINED LIGNITE

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INTRODUCTION

A research program has been developed at the University of North Dakota (UND) for the upgrading of northern Great Plains Province Coals to premium fuels. The Department of Chemical Engineering with support of the Office of Coal Research and the Burlington Northern Railroad, has developed a process for solvent refining North Dakota lignite. The solid, low-melting product, solvent-refined lignite, (SRL) has considerable potential for use as a clean burning solid fuel. However, due to its high reactivity, high solubility, low ash, and low sulfur, it is also a reasonable starting material for catalytic hydrogenation to clean liquid fuels. Thus, the Department of Chemistry has been studying SRL hydrogenation, chemistry, and structure.

In this report a series of batch autoclave hydrogenation experiments on SRL are discussed. In these experiments the effect of variations in temperature, pressure, catalyst, and solvent medium are examined. The most important criterion has been the % conversion of SRL to distillable liquids plus gases. However, the SRL and liquid fractions have also been carefully examined by spectroscopic and analytical chemical methods. It is of interest that we can now readily convert SRL to distillable liquids and gases in over 90% conversion.

EXPERIMENTAL

Solvent Refined Lignite (SRL)

The SRL used in these hydrogenation experiments was prepared by the Pittsburg and Midway Coal Company, Kansas City, Mo., from North Dakota Lignite in chilled anthracene oil. The SRL was ground to 100 mesh. It has the following elemental analysis: C, 85.57; H, 5.62; O, 6.99; N, 1.41; S, 0.3; ash, 0.11. (2)

Catalysts

Six catalysts, Co-Mo-0401 T, Co-Mo-0402 T, Ni-4303 E, Ni-4301 E, Al-1404 T, HT-100 E were purchased from Harshaw chemical Company. Catalysts HZ-1 was supplied by Air Products and Chemicals, Houdry Division. Four Harshaw catalysts, Co-Mo-0402 T, Ni-4301 E, Ni-4303 E, and HT-100 E were presulfided by the procedure described by P.M. Yarvorsky and co-workers (3). Stannous chloride was used as neat powder in run 25, and in run 26, it was impregnated on alumina support. The procedure for impregnation was also given in Yavorsky's paper (3). The presulfided catalysts were prepared and used immediately unless specified. Table I describes the catalysts in detail.

Hydrogenation Equipment and Procedures

The hydrogenation reactor employed is a 1-liter Hastelloy C, MagneDrive batch autoclave purchased from Autoclave Engineers, Inc. Erie, Pa.

In most of the experiments, the autoclave was charged with 75 g of SRL, 150 ml of solvent, a catalyst (1, 10, or 50% by weight based on 75 g of SRL) purged of air and pressurized with hydrogen (1000-2500 psi) from commercial cylinders (for pressure higher than 2,000 psi, a hydraulic jack from American Instruments was employed). The reaction mixture was normally stirred overnight, heated slowly to the desired reaction temperature (375°, 425°, 450°C) in about 50-60 minutes and then held at this temperature for a period of 2 hours. The reactor was cooled slowly to about 150°C. It was then depressurized by passing the reaction gas mixture through an acid trap for ammonia removal, and then through two 0°C traps, two -78°C traps and was finally collected in a 200-liter gas bag.

The ammonia was determined by back titration of the excess acid in the acid trap. The gas in the gas bag was immediately analyzed by a dual-column gas chromatograph to determine the amounts of specific gases produced (Table II).

After removal of the gases, the liquid left in the reactor was separated from the catalyst by decantation. The catalyst, after being washed with 40 ml of solvent, was transferred to a Soxhlet extractor and extracted with THF until the solvent was colorless. The THF extract was then distilled up to 260°C at 1 mm. The non-distillable residue was considered as part of the unconverted SRL and added to the total unconverted SRL for conversion calculations.

The liquid fraction from the reaction mixture and the washing solvent were combined and then distilled first at atmospheric, then at reduced pressure (at 1 torr). When THF was used as a solvent, the reaction mixture was first distilled up to 135° at atm. pressure to remove the solvent, and then vacuum distilled up to 260°C at 1 torr. When tetralin was used as the solvent, the reaction mixture was distilled up to 200°C at atmospheric pressure and then continued at a pressure of 1 torr to yield the following fractions: initial boiling point (IBP)-89°, 89-139°, 139-200°, 200-260°C, and above 260°C (the vacuum bottom). The fraction with a boiling point higher than 260°C at 1 torr was considered to be unconverted SRL. Total conversions were calculated from the unconverted SRL. These distillation and conversion data are tabulated in Table III. We did not list the atmospheric and the first vacuum distillation fractions because they consisted of mainly solvents and a little of the lower boiling liquid which was derived from the cracking of either the SRL or the solvent or both.

In our hydrogenation experiments we have recovered better than 95% of the input material at lower reaction temperatures (375 and 425°C). However, at higher reaction temperature (450°C) the percent recovery was lower (about 93%). The missing material is due partly to the loss through handling and partly to error in the absolute determination of the gas content. By our gas analysis technique we can only determine the absolute amount of methane, ethane, nitrogen, and hydrogen gas in the gas bag. At lower reaction temperatures, little gas was produced, but at higher reaction temperatures the gas production was larger (Table IV).

Product Analyses

The elemental analyses of the distillation and the vacuum bottom fractions are recorded in Table V. The aromatic hydrogen to aliphatic hydrogen ratio was obtained by NMR spectroscopy, (Table V), and phenol and basic amine content (Table V) by titration. The carbon and hydrogen analyses were performed in our laboratory in semi-microscale (10-20 milligrams sample) in duplicate or triplicate. The analyses were periodically checked with standard samples (benzoic acid, and glucose). The NMR data were taken from a Varian A60 NMR spectrometer. For these spectra the SRL and vacuum bottom solids were normally dissolved in deuterated pyridine and the liquid samples in deuterated chloroform. For the solubility determinations of SRL and vacuum bottoms, a 0.15-2.0 g sample was stirred in 30 ml of benzene for 30 minutes, and then filtered. The filtrate was evaporated to dryness. The residue was weighed, and the solubility was calculated, Table V. The basic amines were titrated with 0.1 molar perchloric acid in a mixture of 50 ml of nitrobenzene and 5 ml of glacial acetic acid, and the end points were determined by potentiometric techniques (4). The phenols were titrated potentiometrically with 0.1 molar tetrabutyl-ammonium hydroxide under nitrogen atmosphere in pyridine solvent (5).

The liquid product composition analyses were performed by Gulf Research and Development Company, Pittsburgh, PA (run 31 only). The results are present in Table VI.

RESULTS AND DISCUSSION

A total of thirty-six batch autoclave hydrogenation experiments were performed to determine the effect of solvents, catalysts, temperature, and pressure on conversion of SRL to distillable liquid and gases. The NMR, elemental analysis, titration and solubility of vacuum bottoms data were obtained to give insight into the nature of the hydrogenation reactions.

I. Solvent Studies

It is best if no solvent were to be used for the conversion of SRL into liquids. Practically the results illustrate that the yields are just too low when no solvents are used. Presumably the solvent has several roles during the hydrogenation which are helpful to the reductions. Most important it can function as a hydrogen carrier from the catalyst surface to the material to be reduced. It's secondary function is to cause the mixture to attain a fluid state at the reaction conditions.

In our intial hydrogenation experiments, tetrahydrofuran (THF) and tetralin were used as solvents. THF was employed because it dissolves both the SRL and hydrogenation product, and can be removed easily. Tetralin was used because of its well-known hydrogen donating ability (6) and its higher critical temperature. The conversion data of runs 1, 6 and 44 of Table III show that tetralin is a better solvent in terms of high conversion in the absence of a catalyst (tetralin, 40% and THF, 13-17.5%).

We have also compared naphthalene with tetralin in run 39 and 35, respectively. The conversion data again reveal that tetralin is a better starting solvent (tetralin, 88% and naphthalene, 66%). The ideal solvent is no solvent. However, this appears impractical as the experiments illustrate. The minimum solvent: SRL ratio was next to be established. Runs 41 and 42 were performed with presulfided Ni-Mo-Al_2O_3 catalyst at 450°C with a maximum pressure of 4150 psi, in the absence of a solvent. The conversions were 50%. Under similar conditions, with 150 ml of tetralin a conversion of 88% was found (run 35). In run 47 with 75 ml of tetralin the conversion was 93%. In run 48 in which the solvent volume was 37 ml, the conversion was 91%. Thus, tetralin is a better solvent than THF and naphthalene, probably due to a combination of its hydrogen donating character and higher critical temperature. The solvent to SRL ratio studies showed that the highest conversion was found when the solvent to SRL ratio was 1:1, but a relatively high conversion (91%) could be obtained with a ratio of 1:2. The lower conversion with larger solvent ratios suggests that the solvent is in competition with the SRL during the hydrocracking process.

II. Catalyst Studies

In these studies, attention has been focussed on available catalysts both presulfided and not which had promise of effectiveness from previous reports. The objective was to obtain high conversions of SRL. In the initial catalyst:SRL ratio determination, all conditions were kept constant except for the amount of catalyst present. From runs 7 and 10 (Table III), the percent conversion of SRL did not change significantly on changing the catalyst concentration from 1 to 10%, i.e., 26 and 27%, respectively. However, there is a significant change from the absence of a catalyst to a 1% concentration, found in runs 1, 6, and 7 with THF as solvent, (i.e., from 12.5-17.5% to 25.7%).

With tetralin as the solvent the catalyst concentrations of 10% (run 15) and 50% (run 16) and an initial pressure of 2500 psi were made. This increase gave an increase in conversion of 41 to 48%. Though a 50% catalyst concentration may not be optimum, as compared to the continuous flow systems in which the catalyst to substrate ratio in the reactor is much higher, this percent ratio was maintained for the remainder of the experiments in order to evaluate the effectiveness of a given catalyst on the weight basis.

The next series of batch autoclave experiments were performed to evaluate several proven commercial catalysts with SRL. The six commercial catalysts are the following: Ni-W-SiO_2-Al_2O_3, Ni-W-Al_2O_3, Co-Mo-Al_2O_3-0401 T and -0402 T, Al_2O_3, Ni-Mo-Al_2O_3. Their compositions are given in Table I. In this series, (runs 16, 18, 19, 20, 21, 22, and 24) the highest conversion (54.5%) was found in run 24 with Ni-Mo-Al_2O_3. The lowest conversion (45.6%) was with Ni-W-SiO_2-Al_2O_3. The others are about 48 to 50% conversions. The lower conversion might be due to the fact that Ni-W-SiO_2-Al_2O_3 is relatively sensitive to nitrogen poisoning (1.4% of N in SRL), while on the other hand, Ni-Mo-Al_2O_3 is less sensitive to nitrogen poisoning (7).

To determine the effect of presulfiding, three of the above catalysts (Ni-W-Al_2O_3, Co-Mo-Al_2O_3-0402 T, and Ni-Mo-Al_2O_3) were presulfided and immediately used for hydrogenation. Among the three catalysts used at reaction temperature of 375°C, presulfided Ni-Mo-Al_2O_3, the best under non-presulfided conditions, allowed the highest conversion of SRL (62.1%, run 32). This is a difference of 7% from the non-presulfided run. For the presulfided Ni-W-Al_2O_3 and Co-Mo-Al_2O_3-0402 T catalysts (runs 27, 28, and 29), there was an increase of 11% and 10% respectively. In run 34, 7.5 g of acid-washed molecular seives was added along with the presulfided Ni-Mo-Al_2O_3 catalyst, and the conversion was about the same as that of Ni-Mo-Al_2O_3 by itself (run 31). In general, the presulfided catalysts provided a 10% increase in conversion. Importantly the volume of lower boiling fractions (distillation fraction 1, 2, and 3 in Table III) were generally larger and the last distillation fraction (fraction 4 in Table III) was smaller than those from the non-presulfided catalyst runs. Figures 1, 2, and 3 demonstrate the fact that all three presulfided catalysts produced greater amounts of lighter distillate than the regular commercial catalyst at the same experimental conditions. Thus the distillation data indicate that the presulfided catalysts promote a more extensive hydrogenation and cracking. Fraction 1 in the graphs of Figures 1, 2, and 3 was obtained by subtracting the sum of fraction 2, 3, and 4 from the total conversion. This fraction includes the gas yields, mechanical loss and products that boil lower than 89°C at 1 torr. Mechanical losses are probably the same for both the presulfided and regular catalyst runs, and therefore for comparison purposes, they are constants.

At higher reaction temperatures (425°C and 450°C) the presulfided Ni-Mo-Al_2O_3 catalyst (runs 31, 35) and Ni-W-SiO_2-Al_2O_3 (runs 33, 43, 46) catalyst (which is known as a dual-function hydrocracking catalyst) has been tested. The distillation data show that the presulfided Ni-Mo-Al_2O_3 catalyst of runs 31 and 35 at both temperatures gave higher conversions than the presulfided Ni-W-SiO_2-Al_2O_3 catalyst of runs 33 and 46 at 425°C, 76% vs 68.5% and at 450°C, 88% vs 84%. In run 45, with reaction temperature of 450°C and with no catalyst, the conversion was only 60%, and therefore a difference of more than 25% was due to the effect of the catalyst (run 35 and 46). Thus, presulfiding the catalysts and a reaction temperature of 450°C are necessary for high conversions.

Zinc chloride is another catalyst which has an interesting activity for both hydrogenation and cracking, and it is of special interest since it appears to be less sensitive to nitrogen poisoning (8). Two runs were carried out at 375°C with this catalyst; run 25 as neat $ZnCl_2$ (10%) powder, and the other, run 26, 6.4% $ZnCl_2$ impregnated on alumina (Harshaw Al-1404 T). Run 25, with neat $ZnCl_2$ powder, gave a 53.5% conversion which is as high as that of Ni-Mo-Al_2O_3 catalyst. The impregnated

$ZnCl_2$ catalyst yielded a lower conversion (47% from run 26). This smaller conversion is perhaps due to a smaller amount of $ZnCl_2$ that was used. Work was discontinued with this catalyst due to anticipated catalyst recovery problems.

A cracking catalyst, HZ-1, from Houdry Catalysts was also tested at 425°C with SRL. The conversion was not as high (52.5%) as those with presulfided catalysts in general (run 36).

Thus far, the presulfided Ni-Mo-Al_2O_3 catalyst is the best catalyst in terms of high conversion of SRL to gaseous and liquid products, and that the presulfided catalysts generally give a higher yield of lower boiling fractions than the non-presulfided type.

III. Pressure Effect

Runs 10, 11, 12, 13, 14, and 15 were performed to study the effect of pressure on conversion of SRL to distillate liquids and gases. In runs 10 and 11, an increase of initial pressure from 1000 to 1800 psi, with THF as solvent, did give an increase in conversion of 27.3% to 38%. However, in the case of tetralin as solvent, there was no significant effect on conversion with an increase in initial hydrogen pressure from 1750, 2060 to 2500 psi (40%, 43%, and 40.9% respectively).

IV. Temperature Studies

Several experiments were carried out to determine the ideal reaction temperature with a relatively high conversion. Runs 32, 31, and 35 were carried out at reaction temperatures of 375°, 425°, and 450° respectively while all other conditions remained constant. The percent conversions increased linearly with reaction temperature as illustrated in Figure 4. The percent conversions are 62% for 375°C, 76% for 425°C, and 88% for 450°C. These results suggest that hydrocracking does not proceed readily until the reaction temperature reaches 450°C.

As the reaction temperature increased, gas production also increased rapidly. The total yields of methane and ethane for reactions at 375°, 425°, and 450°C were 0.40 g, 1.78 g, and 5.48 g, respectively (run 32, 31 35, Table II). The ideal reaction temperature is that where gas production is at a minimum and the total conversion is at a maximum. Perhaps, the ideal case may not be obtainable, but the gas production of 5.48 g is still tolerable, and therefore the reaction temperature of 450°C appears to be most favorable.

V. Analytical Methods for Monitoring Reaction Products

Besides using percent conversion as our guideline to determine the effect of solvents, temperature, pressure, and catalysts on the hydrogenation of SRL, we also used and developed other analytical methods to monitor the extent of these hydrogenations. These methods consist of carbon and hydrogen analyses (Table V), NMR data (Table V), basic amine and phenol determinations (Table V), and gas production (Table II).

The atomic H/C ratios were calculated from hydrogen and carbon elemental analyses. These ratios did not vary too much until run 27 (the presulfided catalyst run) and they appeared to be higher for all the runs with presulfided catalysts (e.g., regular commercial catalyst run, 26, fraction (2) 1.22 (3) 1.00, (4) 0.97 (5) 0.90, and for the presulfided catalyst run 27, fraction (2) 1.45, (3) 1.26, (4) 1.15, and (5) 0.96). Runs 27 to 33 gave the typical high atomic H/C ratios.

We have also analyzed the distillation fractions by NMR spectroscopy. The aromatic to aliphatic ratios reveal the same general trend as found in the atomic H/C ratio studies, that is, the aromatic to aliphatic hydrogen ratios are high for earlier runs (up to run 26) and are low from run 27 to run 34. These data suggest that the presulfided catalysts promote the hydrogenation of the aromatic system in the SRL to a greater extent than the non-presulfided catalysts (e.g., run 18, with the regular commercial catalyst, fraction (2) 0.56, (3) 1.00, (4) 1.15, and run 27 with a presulfided catalyst (2) 0.19, (3) 0.21, (4) 0.24). These results indicate that there is more aliphatic hydrogen in the distillation fractions of the presulfided catalyst runs.

The gas analysis data are tabulated in Table II. The higher reaction temperatures tend to yield a larger amount of gases. This is demonstrated in run 32 at 375°, 21 at 425°, and 35 at 450°C with the total methane and ethane yields of 0.40 g, 1.78 g, and 5.48 g respectively. Our aim was to minimize the gas yield and maximize the liquid yield, and thus the reaction temperature should probably not be much higher than 450°C.

In general, nitrogen compounds are known as catalyst poisoning agents, and therefore we are naturally concerned with the basic nitrogen content in the SRL and in the hydrogenation products. We are also interested in the denitrogenation capability of the catalysts. We have adopted the non-aqueous potentiometric titration method for the determination of the basic nitrogen. The titration data are listed in Table V. Most of the vacuum bottoms were analyzed for basic amines and in some cases, some of the distillation fractions were also analyzed in this way.

In general, titration data indicate that the basic amines in the vacuum bottoms of regular commercial catalyst runs were either about the same as in the original SRL (0.54 meq/g SRL) or slightly below. For the presulfided catalyst runs of Ni-4303 E Co-Mo-0402 T and Ni-4301 E, the titrable amine content remained about the same as the original SRL, but that of the presulfided HT-100 E (Ni-Mo-Al_2O_3) was reduced by 50% or more (run 31, 32, and 34, Table V). Thus, this suggests that NiS-MoS_2-Al_2O_3 is a better denitrogenation catalyst than NiS-WS_2-SiO_2-Al_2O_3 and CoS-MoS_2-Al_2O_3.

The phenolic content of the SRL and its hydrogenated products were also determined by non-aqueous potentiometric titrations. In most cases, the vacuum bottom was titrated for phenols so that the phenolic content could be compared with that of SRL (1.34 meq/g SRL). In general, the phenolic content in the vacuum bottom was much lower than that of the SRL (Table V). It is also interesting to note that the runs with a high conversion usually produced a vacuum bottom with a lower phenolic content.

The compositional analysis for the four distillation fractions from run 31 was carried out by the Gulf Research and Development Company. The results are shown in Table VI. The higher boiling fraction appear to have greater amounts (by weight) of fused aromatic systems. Thus, further reduction is needed.

From the benzene dissolution data, no noticable trend is found as in other analytical methods. One thing worth noting is that the vacuum bottoms are normally more soluble than the original SRL (62.2% for SRL).

The production of water is not too predictable although it seems in general to be higher for the later runs (from run 26 on). The difference in water yield is small and the fluctuation is large. Thus, no constructive conclusion can be drawn.

Thus, to sum up, a series of batch autoclave hydrogenation experiments were performed for converting solvent refined lignite (SRL) to premium liquid fuels. A total of thirty-six experiments were performed to accomplish the following: (1) establish the general conditions for the hydrogenation, (2) survey suitable commercial catalysts, (3) investigate the influence of presulfided catalysts, and (4) study the effect of the reaction temperature and solvent. From the initial runs, we have established the general conditions for the catalyst comparison, that is, an initial hydrogen pressure of 2500 psi, 50% catalyst by weight, 150 ml tetralin, and 375°C for reaction temperature. For these conditions, a total of eight catalysts were tested with SRL. The best two of these runs are Ni-Mo-Al_2O_3 (Harshaw HT-100) and stannous chloride catalysts for high conversion of SRL to products. The next series of batch autoclave experiments utilized presulfided catalysts. Result showed that Ni-Mo-Al_2O_3 catalyst still gave the highest conversion. The reaction temperature studies demonstrated that the percent conversion of SRL to distillable liquid and gases increases linearly with the increase of reaction temperature, with a high of 88% conversion at 450°C. From the solvent experiments, tetralin is shown to be necessary for the high conversion. Thus, the experimental conditions for the highest conversion, thus far attained, are the following: initial hydrogen pressure of 2500 psi, 75 g of SRL, tetralin, presulfided HT-100 catalyst, at 450°C for 2 hours.

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TABLE I

Catalysts Used in SRL Hydrogenation

Catalyst	Supplier	Trade Name	Composition Wt. pct.	Pore Vol. cc/g	SA m^2/g	Shape
Co-Mo-Al_2O_3	Harshaw	Co-Mo-0401 T	3 CoO, 9 MoO_3	0.40	160	1/8" tablets
Co-Mo-Al_2O_3	Harshaw	Co-Mo-0402 T	3 CoO, 15 MoO_3	0.40	200	1/8" tablets
Ni-W-Al_2O_3	Harshaw	Ni-4303 E	6 Ni, 19 W	0.54	152	1/12" extrudates
Ni-W-SiO_2-Al_2O_3	Harshaw	Ni-4301 E	6 Ni, 19 W	0.37	228	1/12" extrudates
Al_2O_3	Harshaw	Al-1404 T	97 Al_2O_3	0.42	180	1/8" tablets
Ni-Mo-Al_2O_3	Harshaw	HT-100 E	3.8 Ni, 16.8 Mo	0.54	190	1/16" extrudates
Zeolite	Houdry	HZ-1	45 Al_2O_3,53SiO_2	--	100-150	0.2" pellets

TABLE II

Gas and Water Production

Run	Methane, g	Ethane, g	Ammonia, g	Water, g
16	0.27	0.09	--	1.6
18	0.19	0.13	--	1.6
19	--	--	--	1.8
20	0.21	0.08	--	1.7
21	0.13	0.04	0.01	1.7
22	--	--	0.01	1.6
24	--	--	0.24	1.4
25	--	--	0.01	1.7
26	0.28	0.18	0.08	2.1
27	0.22	0.20	0.33	4.9
28	--	--	0.35	--
29	0.17	0.07	0.19	2.5
30	--	--	0.36	1.9
31	1.10	0.68	0.45	1.2
32	0.27	0.13	0.41	1.4
33	1.27	0.64	0.26	1.5
34	0.81	1.04	0.56	2.1
35	2.14	3.34	0.59	3.3
41			0.30	3.0
43			0.27	2.0
46			0.32	2.5

TABLE III

Tabulation of Hydrogenation Data

Run	Reaction Conditions[1] H_2, Press., psi initial	max.	Solvent 150 ml.	Catalyst[2]	Reaction °C	Distillation of Fractions Wt. % of SRL 1[3]	2	3	4	5	Total Conversion Wt. %
1	900	2600	THF	none	375		→	→	25.3	82.5	17.5
6	1000	2800	THF	none	375		→	→	27.3	87.5	12.5
7	1000	2450	THF	1% Co-Mo-0401 T	375		→	→	32.0	74.3	25.7
10	1000	2600	THF	10% Co-Mo-0401 T	375		→	→	25.5	72.7	27.3
11	1800	2850	THF	10% Co-Mo-0401 T	375		2.0	→	35.6	62.0	38.0
12	1750	2800	Tetralin	10% Co-Mo-0401 T	375		3.3	→	28.8	58.7	41.3
13	1750	2800	Tetralin	10% Co-Mo-0401 T	375		2.0	→	32.8	59.7	40.1
14	2060	3300	Tetralin	10% Co-Mo-0401 T	375		2.1	19.6	12.0	57.3	42.7
15	2500	4100	Tetralin	10% Co-Mo-0401 T	375		2.1	20.5	11.3	59.1	40.9
16	2500	4210	Tetralin	10% Co-Mo-0401 T	375		7.5	19.5	11.7	52.1	47.9
18	2500	4300	Tetralin	Ni-4303 E	375	14.6	4.5	12.8	16.8	51.3	48.7
19	2500	3650	Tetralin	Co-Mo-0402 T	375	13.8	5.5	16.4	14.3	50.0	50.0
20	2500	4100	Tetralin	Co-Mo-0402 T	375		5.5	16.7	14.3	50.5	49.5
21	2500	4400	Tetralin	Ni-4301 E	375		4.4	14.0	16.8	54.4	45.6
22	2500	4500	Tetralin	Al-1404 T	375		4.1	13.5	15.2	50.8	49.2
24	2500	4160	Tetralin	HT-100 E	375	17.8	5.6	17.6	15.5	45.5	54.5
25	2500	3950	Tetralin	10% $SnCl_2$	375		5.2	20.7	9.3	46.5	53.5
26	2500	4150	Tetralin	6.4% $SnCl_2$-Al_2O_3	375		5.7	18.8	14.9	53.1	46.9
27	2500	4150	Tetralin	Ni-4303 E[4]	375	15.8	3.3	20.0	10.7	36.1	59.8
28	2500	4100	Tetralin	Ni-4303 E[4]	375		9.9	19.1	12.7	36.8	57.8
29	2500	4050	Tetralin	Co-Mo-0402 T[4]	375	18.3	10.5	19.5	11.3	40.4	59.6
31	2500	4200	Tetralin	HT-100 E[4]	425		14.0	21.3	11.5	24.3	75.7

TABLE III (continued)

Run	Reaction Consitions[1] H_2, Press., psi initial	max.	Solvent 150 ml.	Catalyst[2]	Reaction °C	Distillation of Fractions Wt. % of SRL 1[3]	2	3	4	5	Total Conversion Wt. %
32	2500	4100	Tetralin	HT-100 E[4]	375	18.3	9.6	22.1	12.1	37.9	62.1
33	2500	4300	Tetralin	Ni-4301 E[4]	425		10.1	21.5	10.4	31.5	68.5
34	2500	4100	Tetralin	HT-100 E[4,5]	425		18.0	17.5	8.4	23.1	76.9
35	2500	4300	Tetralin	Ni-4301 E[4]	450		17.1	15.2	6.8	11.7	88.3
36	2500	4160	Tetralin	HZ-1	425		4.1	18.0	17.1	47.5	52.5
39	2500	3900	Naphthalene	HT-100 E[4]	450		5.6	19.0	14.0	34.4	65.6
41	1750	4000	none	HT-100 E[4]	450		3.7	→	5.4	50.0	50.0
42	1700	4000	none	HT-100 E[4]	450		4.4	→	4.7	50.5	49.5
43	2500	4550	Tetralin	Ni-4301 E[4,6]	450		17.8	13.0	8.0	20.4	79.6
44	1000	1800	Tetralin	none	375		→	→	38.2	60.0	40.0
45	2000	4150	Tetralin	none	450		6.8	22.6	17.3	40.0	60.0
46	2500	4650	Tetralin	Ni-4301 E[4]	450		12.0	17.0	16.5	16.3	83.7
47	2500	4500	75 ml Tetralin	HT-100 E[4]	450		18.1	14.4	4.1	7.4	92.6
48	2100	4500	37 ml Tetralin	HT-100 E[4]	450		12.3	14.0	5.3	8.8	91.2

1 In every hydrogenation experiment, 75 g of SRL was used, and the reactions were kept at the reaction temperature of two hours.

2 The catalyst used was 50% by weight of 75 g SRL unless specified.

3 Fraction 1 in this table was calculated by subtracting the sum of fraction 2, 3, and 4 from the total conversion. Thus, fraction 1 includes mechanical losses, gaseous products, and light distillates.

4 The catalyst was presulfided before used.

5 Acid washed Molecular Sieves 5A (7.5 g) was added.

6 This presulfided catalyst was 4 days old.

TABLE IV. Mass Calculations

Calculation of input and output of the hydrogenation autoclave

		Run 27	Run 31	Run 35
Input:	SRL	75.0	75.0	75.0
	Tetralin	145.5	145.5	145.5
	Catalyst	43.1	40.5	40.6
	H_2	10.8	10.8	10.8
	Tetralin wash	38.8	38.8	38.8
	Total	313.2	310.6	310.7
Output:	Raw Material (hydrogenation products)	228.6	233.4	210.1
	Catalyst	64.0	62.8	60.3
	Autoclave cold traps	1.1	0.0	3.3
	Adhere to autoclave	1.0	1.2	1.0
	Gases from reaction	7.1	7.5	14.5
	Total	301.8	304.9	288.2
% recovery		96.4%	98.2%	92.7%

TABLE V

Tabulation of H/C Ratio, Aromatic to Aliphatic Hydrogen Ratio, and Titration Data

Run	Fraction	H/C Ratio	Ar-H/Al-H	Amines[1]	Phenols[1]	Benzene Dissolution, %
SRL		0.75	2.57	0.54	1.34	62.2
10	2	1.357	1.81			
	3	0.963				
	4	0.813	2.82			
	5	0.413		0.09	0.055	---
11	2	---	0.81			
	3	---				
	4	---	1.69			
	5	---	---	0.47	0.73	---
12	2	---	.96			
	3	---				
	4	0.844	1.58			
	5	0.779		0.51	1.09	---
13	2	---	0.69			
	3	---				
	4	---	1.19			
	5	---		0.53	0.96	---
14	2		0.65			
	3	---	1.05			
	4		1.12			
	5			0.58	0.87	---
16	2	1.22	0.53			
	3	1.03	0.98			
	4	1.03	1.09			
	5	0.91		0.57	0.87	69.8

TABLE V Continued

Run	Fraction	H/C Ratio	Ar-H / Al-H	Amines[1]	Phenols[1]	Benzene Dissolution, %
18	2	1.12	0.56			
	3	0.97	1.00			
	4	0.93	1.15			
	5	0.88		0.52	0.97	
19	2	1.11	0.56			
	3	0.98	0.88			
	4	0.91	0.96			
	5	0.78		0.55	0.91	
20	2	1.14	0.50			
	3	1.13	0.82			
	4	0.98	0.91			
	5	0.81		0.56	0.73	71.1
21	2	1.16	0.647			
	3	1.03	1.21			
	4	0.91	0.90			
	5	0.86		0.48	1.32	
22	2	1.02	1.05			
	3	0.84	1.93			
	4	0.82	2.01			
	5	0.85		0.54	1.12	55.1
24	2	1.20	0.44			
	3	1.07	0.67			
	4	0.96	0.76			
	5	0.91		0.45	0.52	78.4

TABLE V Continued

Run	Fraction	H/C Ratio	$\frac{Ar\text{-}H}{Al\text{-}H}$	Amines[1]	Phenols[1]	Benzene Dissolution, %
25	2	1.24	0.42			
	3	1.31	0.76			
	4	1.04	0.80			
	5			0.46	0.66	82.9
26	2	1.22	0.48			
	3	1.00	0.81			
	4	0.96	0.88			
	5	0.90		0.36	0.66	94.9
27	2	1.46	0.19			
	3	1.26	0.21			
	4	1.15	0.24			
	5	0.96		0.41	0.47	85.3
28	2	1.42	0.16			
	3	1.25	0.23			
	4	1.16	0.27			
	5	0.92		0.49	0.45	81.9
29	2	1.40	0.21	0.19	0.08	
	3	1.17	0.32	0.21	0.16	
	4	1.06	0.42	0.25	0.24	
	5	0.87		0.53	0.79	67.9
3.0	2	1.34	0.40			
	3	1.17	0.39			
	4	1.03	0.54			
	5	0.90	0.65	0.16	0.33	

TABLE V Continued

Run	Fraction	H/C Ratio	$\frac{Ar-H}{Al-H}$	Amines[1]	Phenols[1]	Benzene Dissolution, %
31	2	1.37	0.18			
	3	1.25	0.30			
	4	1.14	0.37			
	5	1.02	0.45	0.20	0.32	87.6
32	2	1.40	0.14			
	3	1.32	0.18			
	4	1.17	0.23			
	5	1.01	0.2	0.23	0.23	86.4
34	2		0.19			
	3		0.33			
	4		0.34			
	5			0.28	0.27	

[1] The basic amines and Phenols are expressed as meq. per gram of SRL or other distillation fractions.

TABLE VI

CHARACTERIZATION OF HYDROGENATED SOLVATED LIGNITE PRODUCTS

	Run 31-2	Run 31-3	Run 31-4	Run 31-1
Boiling Range [1]	87°C (189°F)- 139°C (282°F)	139°C (282°F)- 200°C (392°F)	200°C (392°F)- 260°C (500°F)	IBP- 200°C (392°F)
	Saturates			
Wt% of Sample	12.5	8.6	3.6	73.5
Paraffins	0.4	1.9	1.5	0.0
Non Condensed Cycloparaffins	3.5	0.9	0.8	56.8
Condensed Dicycloparaffins	3.8	2.9	0.7	16.7
Condensed Tricycloparaffins	4.2	2.9	0.6	0.0
	Aromatics			
Wt % of Sample	86.5	90.6	96.2	24.0
Alkylbenzenes	1.1	0.7	2.0	6.8
Indanes/Tetralins	16.6	4.1	3.2	16.0
Naphthalenes	4.9	2.3	1.7	0.5
Phenanthrenes	0.9	0.9	0.0	0.0
Hydrophenanthrenes	30.3	23.6	4.9	0.0
Pyrenes	1.6	9.1	20.0	0.0
Hydropyrenes	16.2	40.0	36.1	0.0
Acenaphthenes/Biphenyls	1.4	0.0	0.0	0.0
Chrysenes	1.4	3.9	12.6	0.0
Benzopyrenes	0.2	1.9	6.4	0.0
Naphthols	2.5	1.0	1.6	0.0
Resorcinols	3.6	0.4	0.6	0.1
Phenols	6.2	2.6	5.1	0.6

[1] Fractions s, 3, and 4 were distilled at 1 torr, and fraction 1 was at atmospheric.

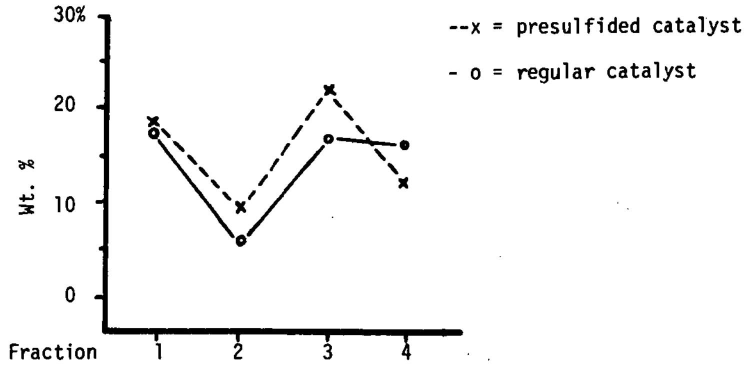

Figure 1. Comparison of distillation fractions from Ni-Mo-Al_2O_3 catalyst.

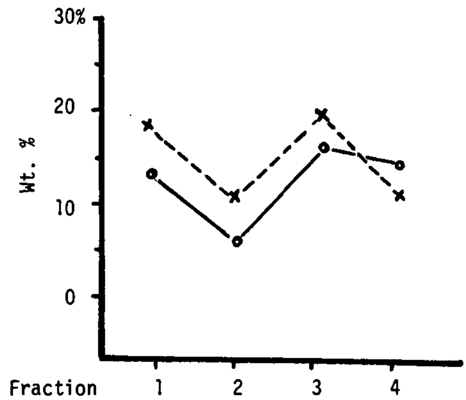

Figure 2. Comparison of distillation fractions from Co-Mo-Al_2O_3-0402 T catalyst.

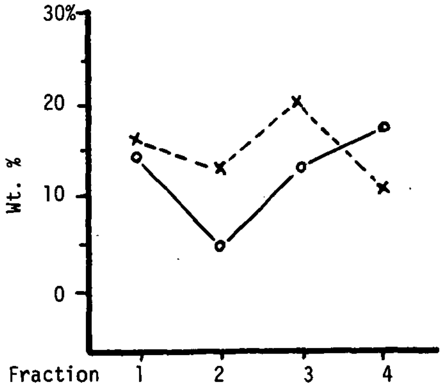

Figure 3. Comparison of distillation fractions from $Ni\text{-}W\text{-}Al_2O_3$ catalyst.

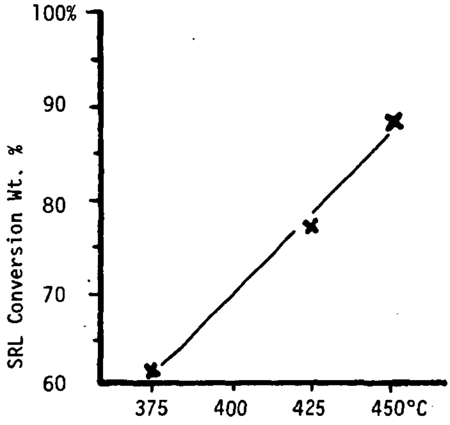

Figure 4. Percent Conversion vs. Reaction Temperature For Presulfided HT-100 Catalyst.

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THE CHARACTERIZATION AND UPGRADING OF COAL LIQUIDS TO HIGH VALUE FUELS AND CHEMICALS. H. P. Malone Gulf Research & Development Company, P.O. Drawer 2038, Pittsburgh, Pa. 15230

The Gulf coal liquefaction process (CCL) catalytically converts coal to commercially and environmentally acceptable liquid fuels. The object of the present work was to study the upgrading of CCL liquids to higher fuels and chemicals.

This study involves characterizing and upgrading CCL liquids to higher value fuels and chemicals.

Liquids from both subbituminous and bituminous coals were separated into naphtha, middle distillate and gas oil fractions. Each fraction was analyzed and its chemical and physical properties determined. The fractions were found to contain a unique distribution of naphthenic, aromatic, and hydroaromatic components. Each fraction also contains some remaining sulfur and nitrogen contaminants and the oxygen concentration is high.

The following processing schemes were used to upgrade these fractions: (a) Naphtha-Mild hydrotreating; (b) Middle Distillate-Mild hydrotreating and hydrocracking, (c) Gas Oil-Severe hydrotreating.

Reforming feedstock, aromatics, kerosene, and low gravity furnace oils were obtained from these processing schemes.

COAL LIQUEFACTION I. CATALYST POISONS PRESENT IN COAL

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INTRODUCTION

A favorable economic future of coal solvation-hydrogenation technology will depend upon the proper selection of coal feedstocks and upon catalyst life and activity. It is reasonably well established that the reactive character of different coals vary widely in solvation-hydrogenation reactions (1, 2, 3). Some coals appear to have a self-catalytic character (3, 4) while others cause a pronounced deactivation or poisoning of the hydrogenation catalyst (5). In any case, deep hydrogenation to remove organic sulfur from the liquid product will require a catalyst (4, 6). The present maximum catalyst life for certain coal liquefaction processes is of the order of 30 to 90 days. The causes for these varying rates of catalyst deactivation are not clearly understood. These effects are believed to be associated with the various coal characteristics including the nature and concentration of minerals or trace elements in the respective coals, or to large phorphyrin type molecules that fill the catalyst pores and hence cause reduced activity.

Previous investigations of coal liquefaction processes employing a heterogeneous catalyst in a solvation-hydrogenation system have reported catalyst deactivation within the time limits previously mentioned. Catalyst activity is measured by the amount of unconverted coal and by product distribution. As the amount of unconverted coal increases and product distribution shifts to the heavier ends the catalyst is described as being deactivated. At this point in these prior studies the catalysts were removed and analyzed as to surface area, pore size and volume and metals on catalyst. In most cases, surface area and pore structure decreased dramatically with a large pickup of metals on the catalyst surface from the coal ash. Catalyst deactivation has been attributed primarily to these metals, and theories advanced on alkali metal poisoning such as sodium, calcium, magnesium; acidic component poisoning such as boron, titanium, and silica-alumina; and the poisoning effects of iron on hydrogenation metals.

It was felt by the authors that the conversion of coal to coal liquids in such a process is a combination of three mechanisms, namely, thermal, hydrogen donor, and heterogeneous catalysts, and that catalyst activity and deactivation was being masked by the gross effects of this process. To better understand catalyst deactivation a more sensitive method for measuring catalyst activity and decline was required. Since metals disposition on the catalyst surface was occurring throughout the process period and at different rates, this more sensitive technique should allow faster and more accurate catalyst activity measurements. A system was devised for this experimental study to expose the catalyst to a coal-ash-donor solvent system and then isolate the catalyst for activity measurement as related to hydrogenating a pure aromatic hydrocarbon. This pure hydrocarbon is the parent aromatic hydrocarbon for producing this donor solvent.

This paper describes the poisoning effect of the major components present in a Western Kentucky coal on a coal liquefaction catalyst. Their effects on catalyst hydrogenation activity was determined by impregnation techniques and by catalyst exposure to a single inorganic salt in an isolated system. The major inorganic elements studied were sodium, magnesium, calcium, iron, titanium, silica-alumina, sodium silicate and phosphorus.

EXPERIMENTAL

Apparatus

The coal liquefaction experiments and reference standard hydrogenation tests were performed in an Autoclave Engineers 2L magnedrive stirred autoclave. The equipment on this autoclave was standard as received from the factory. The cooling coil was removed, and a special 3/8" drain valve was added to the bottom of the reactor for easy and fast dumping of the reactor product. The entire system was properly manifolded for easy and rapid addition of any liquid feed or gas. Liquid product was collected by passage through a cooling coil, pressure was controlled by a regulating valve, and all gases passed through a H_2S scrubber and wet test meter before venting to the atmosphere.

Refractive indices were measured by means of a Bausch and Lomb Refractometer.

Catalyst surface area and pore size-volume were determined by a Micro-Meretics instrument.

Elemental analysis of catalysts before and after treatment with coal and the poison studied were determined by atomic absorption.

Catalyst samples were suspended in a wire mesh basket attached to the baffle plate supplied by the manufacturer.

Materials

The catalyst chosen for this study was Nalcomo 471. The properties of this catalyst are given in Table 1. This catalyst was chosen because of its extensive use by researchers in earlier studies.

The coal utilized in this project was a Western Kentucky #11 from the Fies Mine, its properties are given in Table 2. This coal was received as run of the mine (large lumps) and stored in double plastic bags inside of a sealed metal can. The coal was crushed, sieved and quartered to pass through a 200 mesh screen as needed. Prior to use the coal was dried in a vacuum oven at 100°C.

The reference standard utilized in our hydrogenation tests to measure catalyst activity is a naphthalene-alkylnaphthalene mixture. The properties of this feed are given in Table 1.

Test Procedure

A given weight of catalyst was charged to the catalyst basket in the autoclave, the autoclave was sealed and pressure checked at 2500 PSIG. After a successful pressure check the unit was depressured to atmospheric pressure and repressured to 250 PSIG with hydrogen sulfide and heatup started. The catalyst was presulfided at the gas cylinder pressure and 700°F for three hours. After presulfiding the unit was depressured to atmospheric pressure and the temperature dropped to 250°F. At these conditions 1000 cc of tetralin was added followed by coal addition (300 grams) with stirring. The autoclave was then sealed, pressurized to 2000 PSIG with hydrogen and heated to the operating temperature (650 to 775°F). This heat up period required 60 to 90 minutes.

At the end of the coal liquefaction test, which lasted from six to eight hours; stirring was stopped, and hydrogen pressure was shut down. The product was dumped and collected. As the pressure was reduced all gases in the reactor were passed through a cooling coil to collect condensibles.

To remove any traces of heavy hydrocarbons, the catalyst and vessel were washed once with tetralin and once with the reference hydrogenation feedstock at reaction temperature and pressure. This concluded the first coal run of a test series on the same catalyst charge.

The next step in the test procedure was to measure catalyst hydrogenation activity of the aromatic hydrocarbon standard. Prior to the start of the hydrogenation activity test, the autoclave was preheated to 720°F. Upon the addition of 1000 cc of the reference feedstock (Table 1) and pressuring to 2000 PSIG with hydrogen with stirring, the temperature of the contents of the autoclave dropped to 650°F ±5°F which then became the operating temperature of the standard test. At fifteen minute intervals small samples of the hydrogenated feedstock are withdrawn for refractive index measurement. This allows us to obtain a rate of RI decrease and can determine the exact time required to reach the desired point of hydrogenation. The decrease desired is lowering the index from 1.5877 to 1.5700. This represents approximately a 50% conversion of bicyclic aromatics to the corresponding tetralins. After the hydrogenation test is completed, the unit is prepared for the next coal run by following the test procedure outlined after catalyst presulfiding. This sequence of performing a coal liquefaction run followed by the catalyst hydrogenation activity test can be repeated on the same catalyst charge. In these experiments it was repeated between three and eight times.

The standard conditions utilized in each series of tests are outlined in Table 3. The poison studies in which the catalyst was exposed to a single element present in the coal ash is similar to the technique employed in the coal and reference hydrogenation tests. In these tests, a single ash component was added to the tetralin, its weight corresponding to its concentration in a typical coal run. An example is the use of calcium carbonate. In a typical coal run, 300g of coal is utilized which analyzed at 23.13% ash and 1.37% calcium oxide. This is prorated to show that 1.8g of calcium carbonate would be present in the ash. The catalyst was exposed to this single element in tetralin at conditions corresponding to that employed in a typical coal run. Catalyst washing and the reference feedstock hydrogenation tests are identical to those previously described.

RESULTS AND DISCUSSION

The apparent deactivation of heterogeneous catalysts employed in coal liquefaction processes (solvation-hydrogenation) is rapid when compared to the use of the same catalyst in petroleum processes. This deactivation rate varies depending upon condition, type of coal, etc. (Figure 1). The cause of catalyst deactivation has been attributed by other researchers to metals poisoning. Analysis of their spent catalysts has shown the presence of high concentrations of alkaline and alkaline earth metals, acidic metal oxides, and iron. However, catalyst activity in these studies was measured by the amount of unconverted coal and product distribution (light vs. heavy ends). We felt that catalyst activity as measured in these systems was being masked by the gross effects of the overall process. That is, coal was being converted to liquids by the three previously mentioned mechanisms operating in any high temperature-donor solvent-heterogeneous catalyst process. To better determine the deactivation mechanism or poisoning elements present, an investigation was instituted to look at catalyst activity during coal liquefaction in the early stages (100-200 hrs.), and to employ a more sensitive test to measure catalyst activity. The best test to measure catalyst activity is the hydrogenation of a pure aromatic hydrocarbon. This test is very sensitive to catalyst poisoning by adsorption or reaction of the hydrogenation metals with other metals present in the reaction media.

Since the coal liquefaction process employs a donor solvent, in this case tetralin, the aromatic hydrocarbon chosen was a methylnaphthalene concentrate (Table 1). Catalyst activity was measured as the time required to hydrogenate this concentrate from the naphthalene to the 50%

tetralin stage. This rate was chosen because at the 50% tetralin stage, the hydrogenation of tetralin to decalin has not occurred which can complicate the rate of reaction (time).

A series of hydrogenation tests were made with the virgin presulfided catalyst and the reference feedstock to establish uncontaminated catalyst activity. A series of six preliminary runs, using the reference feedstock only,established the time necessary to reach the 50% conversion level using the virgin catalyst. A small decline in catalyst activity was recorded between the first two runs. The remaining four runs indicated that an asymptotic value of activity had been reached. The times for these four runs were averaged and this established an equilibrated catalyst activity time of 171 minutes. From these tests initial catalyst activity was determined and assigned a value of catalyst relative activity of 1.0. All other catalyst activities are measured relative to this value and are determined as follows:

$$\text{Catalyst Relative Activity} = \frac{171 \text{ minutes}}{\text{Time (min) to hydrogenate to } 1.5700}$$

Since any significant poisoning of the catalyst by coal constituents will increase Time (1.5700) the denominator will always be greater than 171 minutes. Thus the catalyst relative activity will be between zero and one.

Coal Liquefaction Studies

Based upon our initial premise as to catalyst activity, catalyst deactivation, and liquefaction mechanisms, a series of studies on catalyst activity decline during coal liquefaction were initiated. We anticipated that the initial measurements of catalyst hydrogenation activity would remain high (near 1.0) and would show a slight decline in the region of 50-100 lbs. coal per lb. of catalyst. Beyond this point catalyst activity would decline more rapidly and the rate would determine at what point the catalyst would be removed for analysis. Analysis at this point would consist of surface area and pore size-volume measurements and the determination of any trace elements absorbed on the catalyst surface from the coal ash.

As noted in Figure 2 this never occurred. After many repeat tests to correct operating procedure, and mechanical problems, we finally resolved that catalyst deactivation was occurring in the first test upon exposure to coal. This is shown by the curve for coal liquefaction at 675°F. Additional experiments were made at higher temperatures on the premise that too much heavy material was remaining unconverted and required higher temperatures to be cracked and hydrogenated to less viscous material. The curves for operation at 725°F and 775°F show that initially catalyst activity improved but rapidly decreased with subsequent coal liquefaction runs, and approached (within experimental error) the same ultimate asymptotic value of activity.

At this point it was not known if catalyst deactivation was due to carbon laydown or metals poisoning. Analysis of the catalyst by X-ray diffraction and AA showed only traces of ash components present on the catalyst surface. These were only present in 0.1 wt. % or less concentration which was considered insufficient to decrease catalyst activity any significant amount.

The catalyst was then submitted for surface area and pore volume analysis. The results (Table 5) were more dramatic as to reasons for catalyst deactivation.

TABLE 5

	S.A. M^2/g	P.V. cc/g	% C - Wt. %
Fresh 471	260	0.46	0.0
Used 471 - 675°F	126.5	0.20	18
Used 471 - 775°F	158	0.25	15

These results showed that catalyst deactivation was occurring as soon as the catalyst contacted the coal-solvent system. These heavy carbonaceous materials could include tars, asphaltenes, maltenes, resins, etc. To establish if this theory was correct the catalyst would only need to be regenerated in air to remove the carbon and be restored to virgin activity.

Figure 3 shows the effect of carbon on catalyst and regeneration with air on catalyst activity. The catalyst was contacted with coal for a single pass and its activity measured. It was then regenerated in air at 925°F and its activity measured. This sequence was repeated on the same catalyst with two coal runs in sequence. Regeneration with air again restored the catalyst to virgin activity. The effect of repeated exposure of the catalyst to the coal-solvent system gives catalyst relative activity rates that fall on the original curves shown in Figure 2.

These data show that catalyst hydrogenation activity drops dramatically upon initial exposure to a coal-solvent system. Catalyst relative activity drops to 10-20% of virgin activity when only 20-40 lbs. of coal is processed per lb. of catalyst. Those processes presently showing potential for commercial development that have reported a catalyst operating at a high and constant activity level are in reality operating at a level that is almost near complete deactivation. This is further substantiated by the sudden and rapid decline in activity that they themselves have reported.

<u>Poisons in Coal Ash - Catalyst Impregnation</u>

The next phase of this program was to determine the major elements present in our coal ash (Table 2) and the type of compound they represent. This was tentatively identified by the Chemical Engineering-Geological Department of the University of Kentucky. The first step was to study the effects of these elements on catalyst activity by impregnation. Figure 4 gives the results of these tests.

The elements were impregnated upon the Nalco 471 catalyst through the use of water soluble salts. These salts were typically nitrates or chlorides. As expected, the alkali salts (Na, Ca, Mg) gave the highest degree of deactivation whereas the acidic components (B, Ti, Si) gave little or no deactivation. Secondly, these curves would give a basis for measuring catalyst deactivation when the catalyst was exposed to a single ash compound.

Poisons in Coal Ash - Catalyst Exposed to Single Component

Upon completion of the catalyst poison study by impregnation, the next phase was the exposure of the Nalco 471 catalyst to a single component. This was accomplished by employing tetralin as the solvent and suspending the single compound in the donor solvent as a fine powder (as present in the coal ash during a coal run). The compounds utilized in this series are given in Figures 5 and 6 alongside of the appropriate activity curves. In some cases these activity curves are identical to that obtained for the impregnation tests and in others dissimilar.

The best interpretation of these tests and curves are given in Table 4. The grams of each compound utilized represents its concentration in 300g of coal (amount per test run). After this had been exposed to five repeat runs (the equivalent of 60 lbs. of coal per lb. of catalyst), the catalyst was removed and analyzed for the amount of the particular element tested that had been adsorbed on its surface. This figure is reported as % metal oxide on catalyst - AA. The final activity of the catalyst after the poison study is reported under the column catalyst activity. The final column catalyst activity based on Figure 4 is the catalyst activity as estimated from Figure 4 based upon the amount of the poison (ash constituent) analyzed by AA and reported accordingly.

The basic materials follow fairly close to the activity measurements. The large discrepancies occur in the occlusions of the acidic components.

SUMMARY AND CONCLUSIONS

The liquefaction of coal in a donor solvent-heterogeneous catalyst system leads to catalyst deactivation by two types of poisons. These poisons are of a temporary and permanent type. The temporary poison is a heavy carbonaceous material which acts immediately upon catalyst activity, but activity can be restored to near virgin activity by an air regeneration. The permanent poisons (no known commercial economical method known for its removal) are the components present in coal ash. The degrees of deactivation by these coal ash components on heterogeneous catalysts have been determined and it has been shown that the alkaline materials are more detrimental to catalyst activity than the acidic components.

Our future work will entail studies to find a catalyst that is more active in the presence of these carbonaceous materials.

Also we will determine the rate of deposition of the elements from coal ash on a catalyst and the rate of change of catalyst activity with concentration.

ACKNOWLEDGEMENT

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TABLE 1

NALCOMO 471
(Cobalt-Molybdenum-Alumina)

CHEMICAL ANALYSES, Wt. %

% MoO_3	12.5
% CoO	3.5
% Na_2O	.05
% Fe	.03
% SiO_2	.3

PHYSICAL PROPERTIES

Surface Area, M^2/gm	260
Pore Volume, Cm^3/gm ($C\ Cl_4$)	.46
Density, lbs/ft^3	39
Density, gm/cc	.67
Strength, lbs crush (avg.)	14
*Attrition Index	92
Size	1/16"
Form	Extrudate

* % Retained on a 20 mesh sieve after tumbling one hour.

STANDARD (41 TK) FEED
GC ANALYSIS (Wt. %)

1.	Less than Naph.	9.61
2.	Naphthalene	15.74
3.	Naph-MN	4.06
4.	2-Methylnaph	27.44
5.	1-Methylnaph	13.78
6.	MN-EN	0.41
7.	2-Ethylnaph	1.91
8.	Biphenyl	-----
9.	1-Ethylnaph	0.66
10.	2,6 + 2,7 DMN	5.60
11.	1,7 DMN	2.60
12.	1,3 + 1,6 DMN	7.33
13.	2,3 + 1,4 DMN	2.18
14.	1,5 DMN	0.91
15.	1,2 DMN	1.55
16.	Greater than DMN	6.22
	Refractive Index (24°C)	1.5877

TABLE 2

COAL SAMPLE 11-000
#11 MADISONVILLE - FIES MINE
Island Creek Coal Company

	AS RECEIVED	MOISTURE FREE
Moisture	4.68	-----
Ash	22.05	23.13
Volatiles	33.90	35.56
Fixed Carbon	39.37	41.31
Sulfur	3.68	3.86
BTU/lb.	10,390	10,900

ASH ANALYSIS - WT. % ASH	
SiO_2	53.81
Fe_2O_3	12.11
TiO_2	0.89
Al_2O_3	23.48
CaO	1.37
MgO	0.80

TABLE 3

STANDARD CONDITIONS

COAL RUNS

Figures 2 and 3

Temperature ^{o}F	-	As Noted
Pressure	-	2,000 PSIG
Catalyst	-	25g Nalcomo 471
Coal	-	300g
Solvent	-	1,000g Tetralin
Stirring Rate	-	1200 RPM

STANDARD REFERENCE RUNS

MEASURE RELATIVE ACTIVITY OF CATALYST

Figures 2, 3, 4, 5, 6

1,000 cc of 41 TK Feed

Pressure	-	2,000 PSIG
Temperature ^{o}F	-	$650^{o}F$
Stirring Rate	-	1200 RPM
Catalyst	-	25g Nalcomo 471

POISON STUDIES

Figures 5 and 6

Temperature ^{o}F	-	$675^{o}F$
Pressure	-	2,000 PSIG
Solvent	-	1,000g Tetralin
Stirring Rate	-	1200 RPM

Amount of Single Poison Added per run - See Table 4

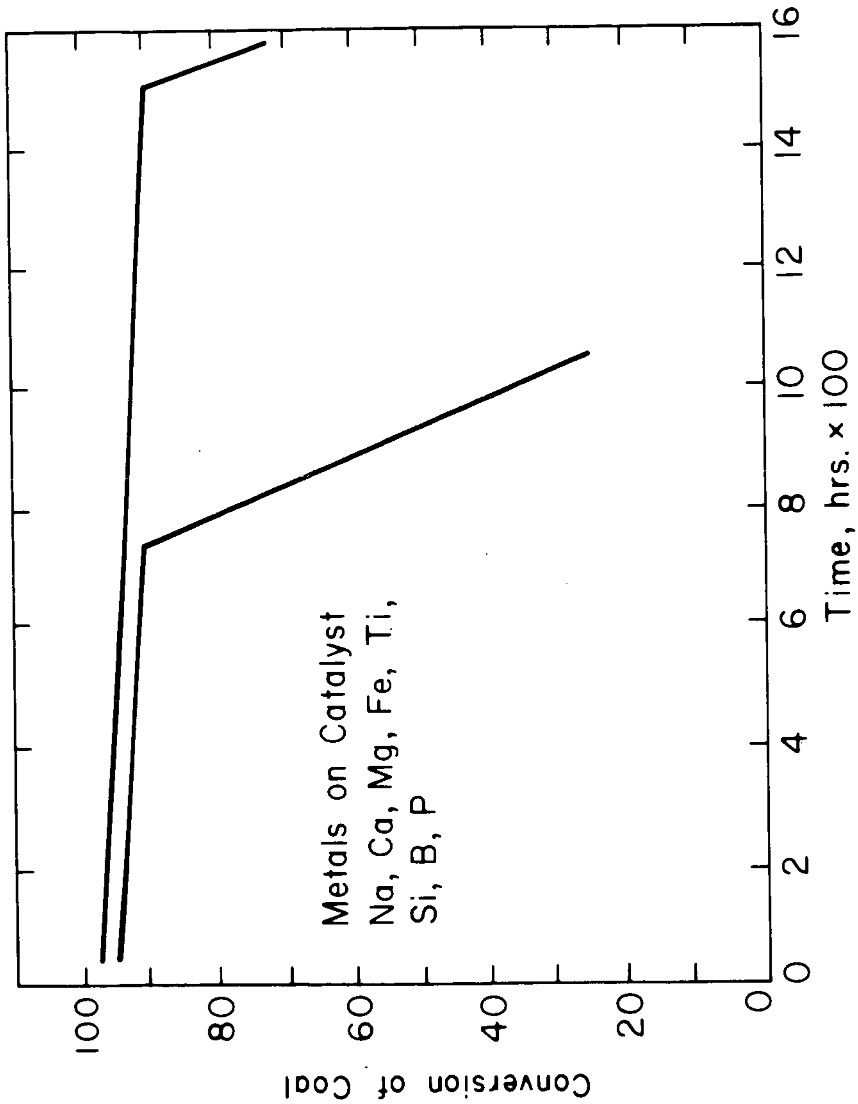

Fig. 1 Catalyst Deactivation

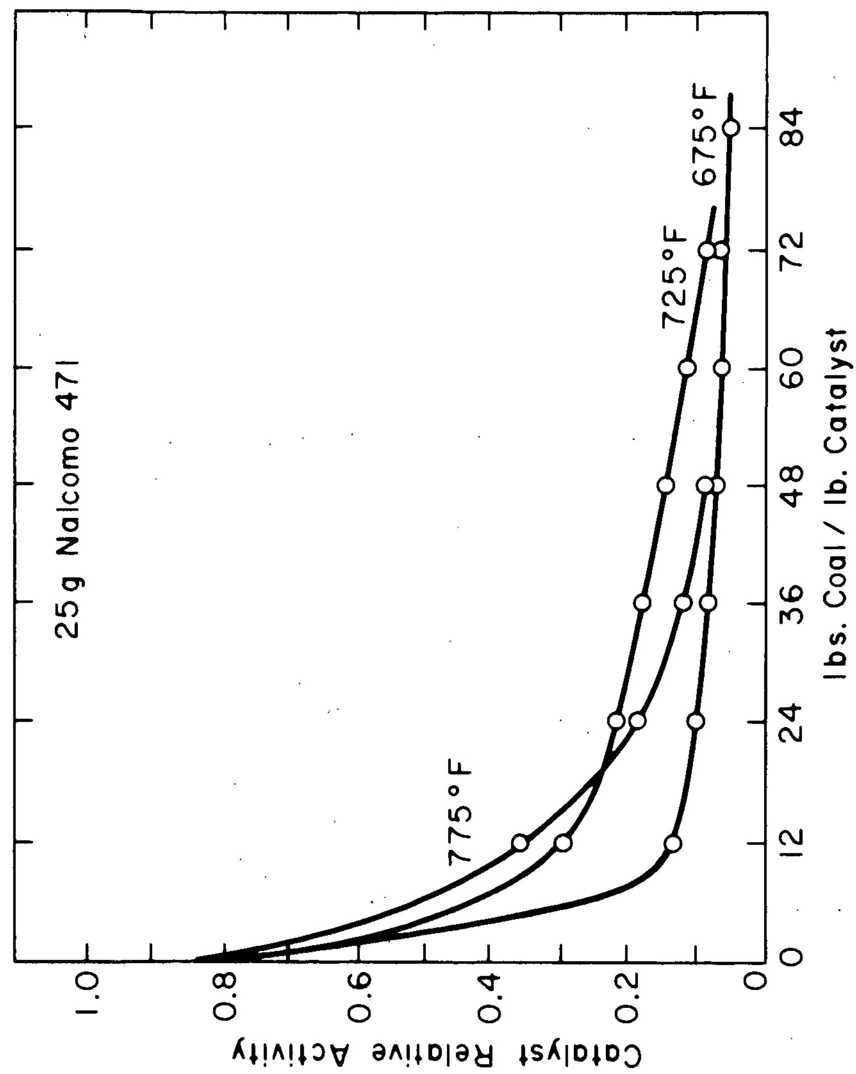

Fig. 2 Effect of Temperature

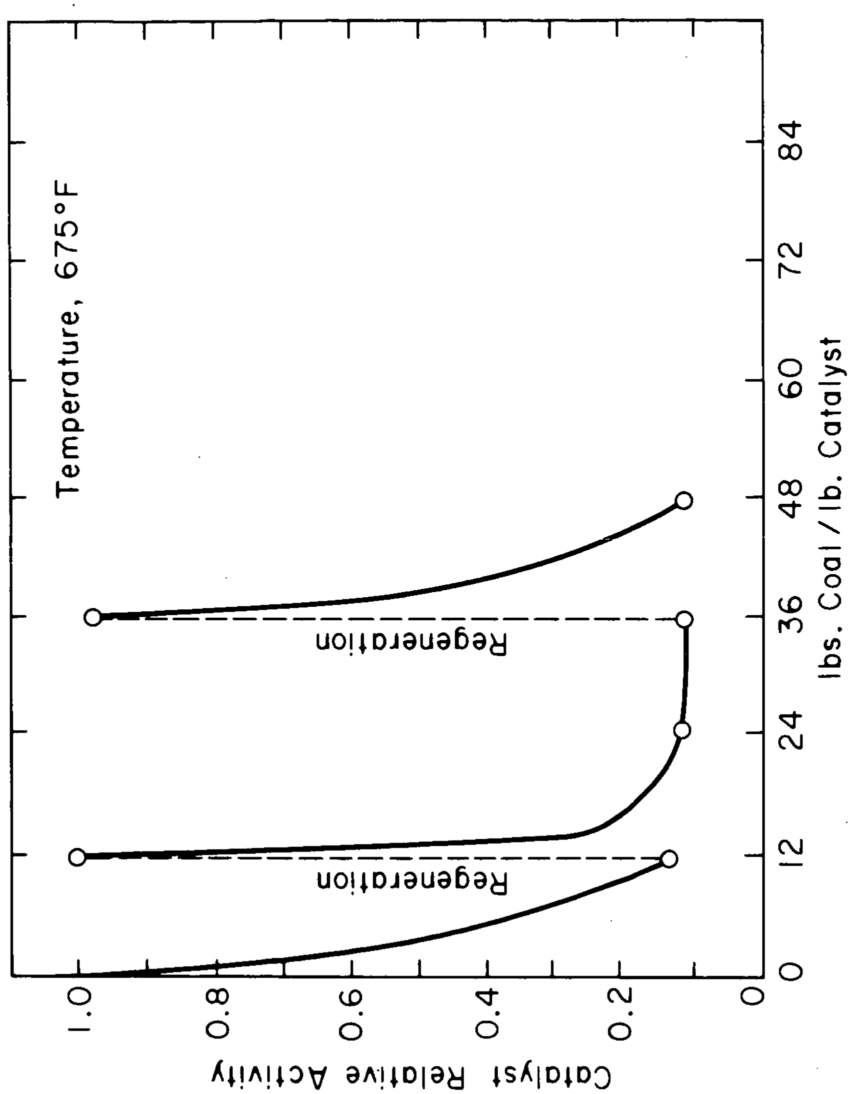

Fig. 3 Effect of Heavy Ends

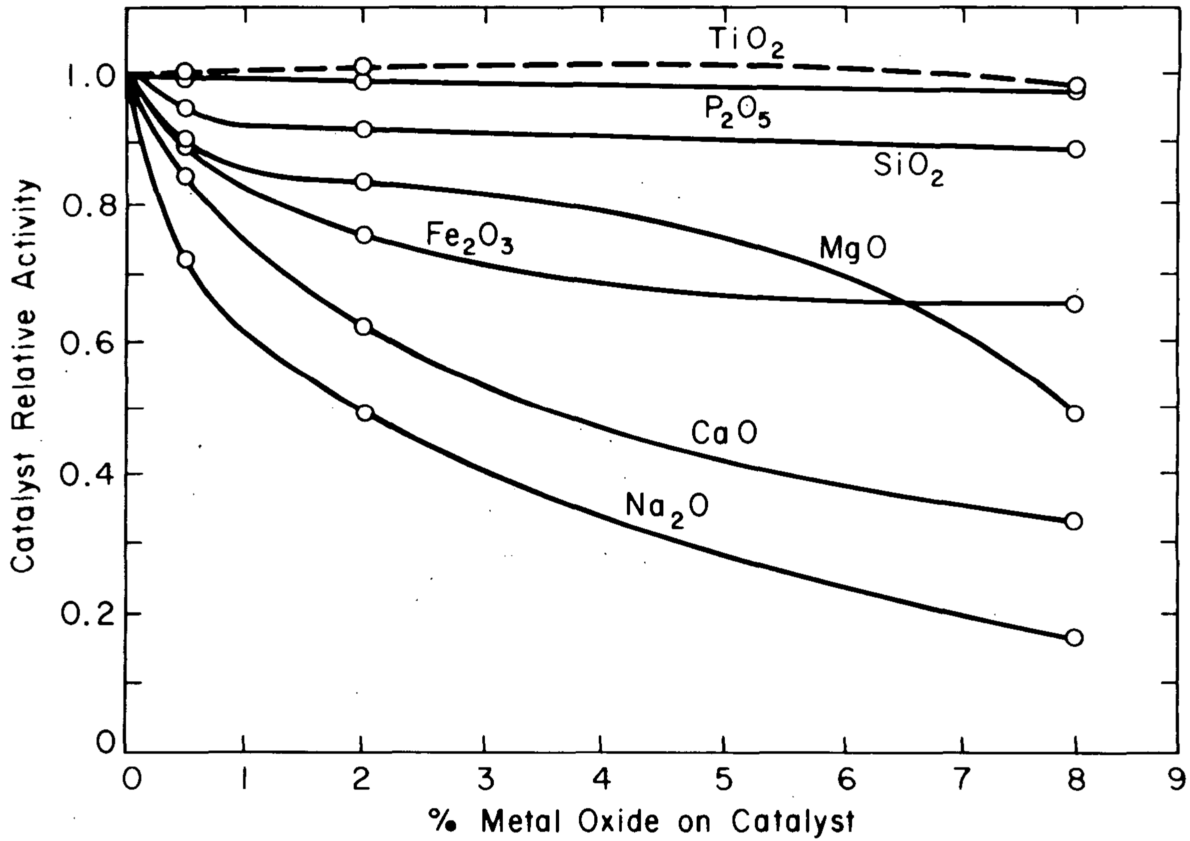

Fig. 4 Single Ash Component by Impregnation

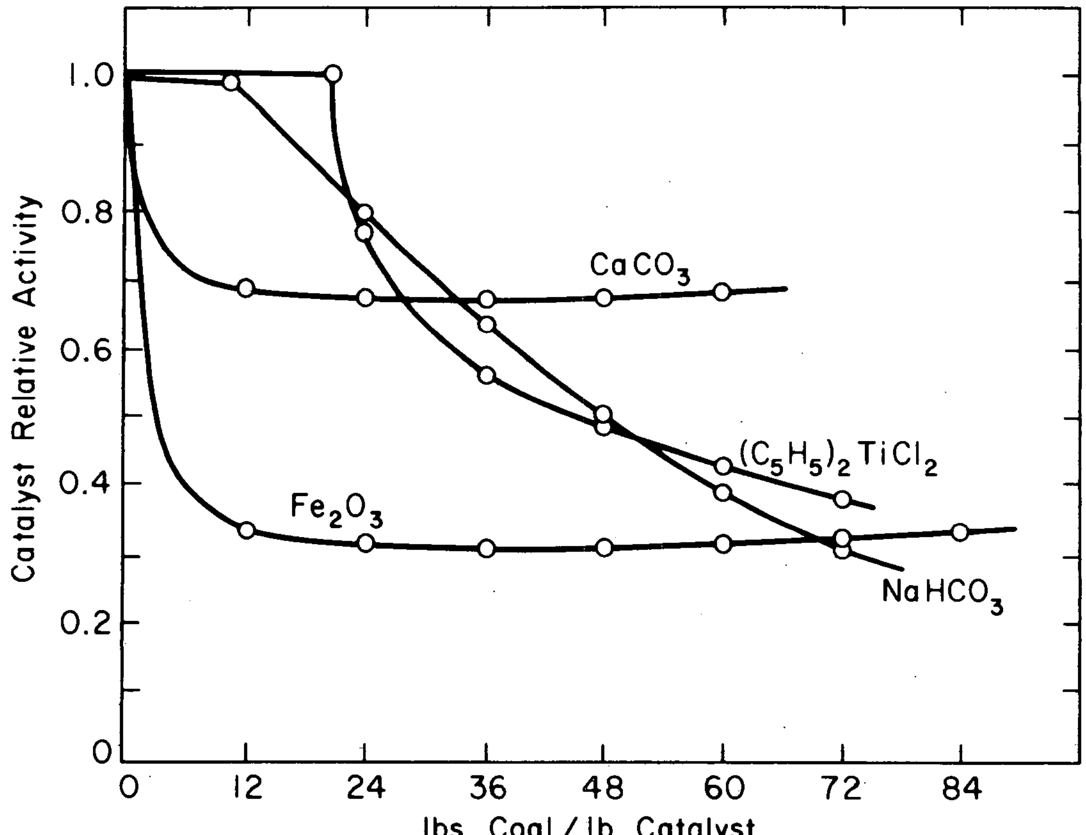

Fig. 5 Catalyst Exposed to Single Ash Compound

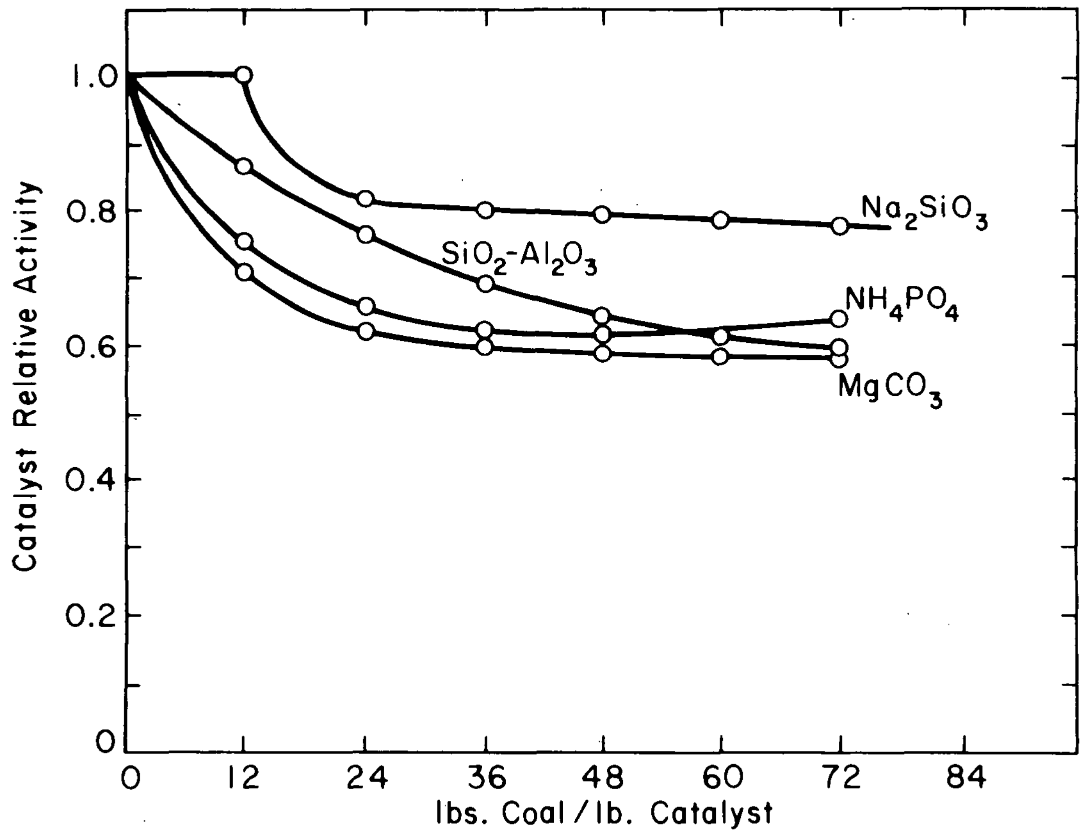

Fig. 6 Catalyst Exposed to Single Ash Compound

TABLE 4

ASH CONSTITUENT	g/RUN	CATALYST ACTIVITY	% METAL OXIDE ON CATALYST-AA	CATALYST ACT. BASED ON FIG. 4
$NaHCO_3$	1.0	0.53	2.2	0.51
$CaCO_3$	1.8	0.69	0.44	0.79
$MgCO_3$	1.3	0.60	3.0	0.72
Fe_2O_3	8.0	0.34	10.0	0.38
$TiCl_2\ (CP)_2$	2.0	0.82 (R)	2.2	0.98
NH_4PO_4	0.5	0.80 (R)		
Na_2SiO_3	1.0	0.75	1.1 Total 0.45 Na	0.9 - SiO_2 0.80 - Na
SiO_2-Al_2O_3	50	0.69	7.3	0.90

(R) = CATALYST REGENERATED IN AIR TO REMOVE CARBON OR AMMONIA

KINETIC MODEL FOR COAL PYROLYSIS OPTIMIZATION

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1. Introduction

Most coal conversion processes, liquefaction as well as gasification, are conducted at elevated temperatures (> 400. C). At these temperatures the coal decomposes to yield volatiles (tars and gases) and a solid residue (char). If this is done in an inert atmosphere then the coal will only pyrolyse. However, if there is a reacting ambient atmosphere (e.g. hydrogen or steam), in addition to the pyrolysis, gasification of the char and reactions of the volatile matter with the reacting gas will occur. Before we can model the complex situation with a reacting ambient gas, a better understanding of the pyrolysis of coal in an inert atmosphere must be obtained .

Most of the conversion processes that have been or are being developed at present are based only on experimental results obtained in bench scale experiments or in so-called process development units. Since these experiments are time and money consuming, the whole range of process parameters can not always be covered. Hence it is never certain whether the optimum conditions for a specific process have been found, after a limited series of experiments. Here a theoretical modeling technique would be a much more efficient way of optimizing the process. Any theoretical model for a pyrolytic coal conversion process would be based on a) a kinetic model for coal pyrolysis and b) a mathematical model of the flow reactor.

The purpose of this study is to establish a chemical kinetic model which later will be coupled with fluid-mechanical models for several flow reactors. This kinetic model should be applicable over a wide range of operating conditions (e.g. temperature, heating rate) in order that the optimization of a new process not be limited by the applicability of the kinetic scheme. The kinetic scheme should be able to distinguish between condensible tars and non-condensing gases, to allow the optimization of either liquefaction or gasification processes.

Our chemical kinetic model will be based on experimental results that have been reported in the literature. However, a number of simplifications will be introduced because the available data do not always contain the specific information that is necessary to obtain kinetic values for our scheme. Since most of the published experimental results are for high volatile A bituminous coals, we limited our attention to such hvAb coals for the first approach.

Before we can postulate a kinetic scheme for coal pyrolysis we have to define the characteristic parameters of coal pyrolysis and specify the range in which these parameters might vary.

The pyrolysis of coal leads to two general products: a) the volatile matter which may be divided into pitch, tar, light oil, gases and carbonization water, and b) solid residue comprising coke or char. Pitch, tar and light oils are often simply lumped together and called tars. The carbonization water includes the ammonia. The product gases account for everything that is gaseous at standard temperature and pressure, such as hydrocarbons (saturated and unsaturated), hydrogen, and oxides of carbon. Pitch is a solid at standard temperature and pressure, but since it leaves the reactor as volatile matter, it is lumped in with the tars.

The variables and their typical range to be considered in the modeling of a coal pyrolysis process for a given coal include:

A) final process temperature (400 C up to above 1000 C)
B) the heating rate or temperature history of the coal (10^{-4} C/sec up to 10^{5} C/sec, corresponding to heat-up times ranging from several months to as short as ten milliseconds.)
C) coal particle size (10 μm up to several mm)
D) pressure in the reactor (1 atm to 50 atm)
E) residence time of the coal and the volatile matter in the reactor, which is dependent on the type of the reactor (e.g. fixed bed counter-flow, entrained-flow, etc.) and the reactor size.

The residence time of the products in the reactor is determined by the bed depth and the flow rate of sweep gas through the reactor. The temperature history of each coal particle is determined by the temperature of the gas and the pressure in the reactor, as well as by the coal particle size. However, for our parametric studies, we will specify a certain heating rate as an independant parameter, and then the gas temperature and the coal particle size needed to best accomplish this temperature history can be selected separately.

2. Review of Previous Relevant Work

A General References

The pyrolysis of coal has received substantial attention for decades but until about 15 years ago most of the work was concerned with coal carbonization and coke production, i.e. coal pyrolysis with slow heating rates and long residence times of the solid material and the volatiles in the hot reactor [1 - 8]. Most of this work was done in fixed bed reactors or in laboratory retorts. The objective was the optimization of the quality and yield of coke. Extensive understanding of the structure of coal and of the products of the carbonization process was obtained through these studies.

Several standard laboratory methods were developed in connection with the pyrolysis processes. These include the Fischer Assay (originally called the Fischer-Schrader Assay, developed in 1920)[45], the Bureau of Mines - American Gas Association Method [6] and the Gray-King Assay. These are used to determine carbonization properties and the volatile matter content of the coal. Each employs slow heating rates with maximum temperatures between 500 and 900 C, with no sweep gas used to remove the pyrolysis products. As a result, none of these can prevent secondary reactions between the volatiles and the coke.

Following the discovery in 1964 by Loison and Chauvin [9] that rapid heating of the coal results in a higher volatile yield than expected on the basis of an ASTM proximate analysis [44], new coal pyrolysis processes have been studied and a better understanding of the process has beeen obtained.

Studies of the pyrolysis process in pulverized coal flames have yielded information on the effects of rapid heating rates [10 - 13]. Small particles (< 100 μm) and heating rates up to $5 \cdot 10^5$ C/sec were used in the reported tests. Meanwhile, interest in coal conversion was growing at this time (mid 1960's) and the objective was now to maximize the tar and gas yields [14 - 17]. These processes are characterized by residence times of the product gases of less than 1 minute and high heating rates of the coal particles. The coal is devolatilized in fluidized beds or entrained beds and a carrier gas is used to rapidly sweep the volatiles out of the reactor.

Several authors have previously proposed different reaction schemes to describe the kinetics of coal pyrolysis. Just as in the general literature on coal pyrolysis, these models can be divided into two classes :

a) Models for slow pyrolysis : heating rate less than 10^{-2} C/sec or low final temperature (< 600 C)

b) Models for fast pyrolysis : heating rate higher than 100 C/sec and high final temperature (> 600. C)

Probably the first chemical model in terms of a complex of chemical reactions was formulated by van Krevelen et. al. in 1956 [1,3]. They proposed the following overall scheme:

I	Coking Coal	$\longrightarrow$	Metaplast
II	Metaplast	$\longrightarrow$	Semi-coke + Primary Volatiles
III	Semi-coke	$\longrightarrow$	Coke + Secondary Gas

They did not incorporate any secondary reactions, although their experimental data were from slow carbonization processes, where secondary reactions certainly occur. Van Krevelen proposed this scheme as a " mathematical model " with many simplifications, but with the potential to explain, at least qualitatively, many of the phenomena observed in a carbonization process. His main concern was the softening of the coal, without being as concerned with predicting yields. He assumed first-order reactions with an Arrhenius type rate law. Because of the simplicity of this model, it gave only qualitative results and was applicable only to a small temperature range and low heating rates.

Hill and Wiser at the University of Utah [18, 19] conducted a series of long duration (up to 10 hours), low temperature pyrolysis experiments. They observed three regions with different reaction orders. In the first 60 minutes the rate of the reaction was approximately of the second order. This period was followed by a first order period for about 100 minutes. The last region was found to be controlled by a zero order rate law. This sequence was interpreted in terms of six chemical reactions, that have been formulated with molecular compounds. This mechanism is based on experimental data for only these slow processes, and it is not applicable to fast processes.

Berkowitz [8] obtained similar data for slow experiments and concluded, that for the conditions of his experiments the rate determining step of the pyrolytic reaction was the diffusion of the volatile matter out of the coal particle. Later, however, Pitt [5] used his own experimental data and the data of Berkowitz to support a chemical model. Pitt interpreted coal as a mixture of many components that can decompose independently, following a first order reaction with a wide distribution of activation energies. Unfortunately, Pitt did not determine the weight loss directly, but used the remaining volatile matter in the char as a measure of the degree of decomposition. Furthermore, he used a fixed, arbitrary frequency factor of $1.6 \cdot 10^{13}$ sec^{-1} in the Arrhenius formula to determine the distribution of the activation energies, which of course is an arbitrary constraint that affects the numerical values of the activation energies.

Between 1960 and 1970, Peters and Juentgen et.al. at the Bergbauforschung GmbH in Essen, Germany [2, 20, 22, 23] did some extensive studies on the gas release of hydrocarbons during very slow carbonization. They found that this gas release can be modeled by many parallel first-order single reactions, i.e. by a first-order reaction complex with distributed activation energies and frequency factors. They postulated that the gas release occurs in a sequence of the following four steps [22]:

A) thermal activation of the coal substance (equilibrium reaction)
B) unimolecular reaction, bond scissions and formation of radicals
C) reaction of two radicals to form a stable molecule
D) diffusion of the molecule out of the particle

Figure 1 is a schematic representation of this process. The aromatic ring with aliphatic side chains represents the coal structure.

Besides these models that deal only with slow processes, some models have been developed that can be applied to a fast pyrolysis process (heating rates 500 C/sec and up).

Kobayashi [24] used the data of Kimber and Gray [13] and Badzioch and Hawksley [11] to develop a kinetic model for the rapid decomposition of pulverized coal particles. His mechanism consisted of two competing first order reactions :

$$C \xrightarrow{I} (1 - x_1)\, S_1 + x_1\, V_1$$

$$C \xrightarrow{II} (1 - x_2)\, S_2 + x_2\, V_2$$

The kinetic values and the heats of reaction for these two reactions are given in Table I (Stickler et.al. found later in high temperature experiments that these heats of reactions are overestimated). This mechanism is applicable only for high heating rates (10^4 C/sec) and high temperatrues (> 1000 K); it does not fit the slow, low temperature pyrolysis data.

Very recently Stickler et.al. [25] applied this scheme to model the gasification of pulverized coal in hot combustion gases. They added a physical gas flow and heat transport model, so that they were able to consider the heat-up of particles of different size classes. They used this model for comparison with experimental results for very high heating rates (10^5 C/sec) and high final temperatures (1700 K - 2300 K). In this limited range of operating conditions they only had a few experimental points to check the accuracy of this scheme.

Anthony wrote (1974) his Ph.D. Thesis on the kinetics of coal pyrolysis and hydrogasification [26]. He conducted experiments over a temperature range of 400 C to 1000 C and with heating rates varying from 10^2 to 10^4 C/sec. He found that the weight loss depends on the final temperature, but not on the heating rate. This led him to conclude that there are no concurrent, widely different competitive reactions. He therefore proposed a multiple reaction model with a statistically distributed activation energy, but with a constant frequency factor. For a bituminous coal he determined $E = 32.7 - 41.1$ kcal/mole and $A = 2.91 \cdot 10^3\ sec^{-1}$ at 1000 psia. He also introduced secondary deposition reactions for a " reactive " part of the volatile matter, which compete with the diffusive escape of the volatiles. He determined the ratio of the reaction rate of the secondary reactions to the overall mass transfer coefficient from experimental results and did not investigate these degradation reactions in detail. Neither Anthony nor Kobayashi, however, made any distiction between tar and gas in the volatile matter.

The numerical values for the kinetic parameters of the reaction scheme (activation energies, frequency factors, and stoichiometric coefficients) proposed in the present study were deduced in part by fitting the theoretical predictions with relevant data reported in the literature. In the present study, attention has been centered mainly on the primary decomposition. Two sets of data were found to be the most suitable for this purpose : Curves obtained by Badzioch and Hawksley [11] at BCURA in Great Britain, and results from Peters and Juentgen [2] of Bergbauforschung GmbH in Essen, Germany. Both research groups made their experiments with several coals of different rank. The results for two hvAb coals have been used in our present study. In the following, the work of these two groups will be discussed in detail.

3 Work Done by Badzioch and Hawksley at the British Coal Utilisation Research Assocation (BCURA)

Badzioch and Hawksley simulated the conditions in a pulverized coal flame, i.e. high heating rates (25000. - 50000. C/sec) and high temperatures (650 C - 950 C). They used pulverized coal with a mean particle size of about 20 μm . The experiments were carried out for ten different coals, from which we chose coal D , which is an hvAb coal with a composition similar to that of coal Fuerst Leopold used by Peters and Juentgen.

The experimental apparatus was a laminar flow furnace, which was heated to the desired temperature and through which a preheated flow of nitrogen was blown. The coal was then injected together with some cold nitrogen (in a dilute flow) into the hot main gas stream. The heat-up of the coal particle was rate-controlled by the mixing of the cold and the hot gases, which was found to take approximately 20 msec (for 20 μm particles, thermal equilibration internally is fast compared with the fluid-mechanical mixing rate). The coal particles were collected and rapidly quenched after travelling a predetermined distance from the injector. This distance controlled the residence time of the particles in the furnace. The weight loss was determined by analysing the solid residue with respect to the ash content and the proximate volatile matter.

The qualitative results are ;

1) The devolatilization products are richer in tars for this fast process than for a slow pyrolysis [10].

2) The weight loss exceeded the proximate volatile matter by a factor of 1.3 - 1.8 , depending on the coal rank.

3) Even though the weight loss curve leveled off after about 100 msec (depending on the temperature) some residual volatile matter was found in the char.

They were able to fit the experimental results with an empirical relation for the weight loss as a function of time and temperature :

$$V = B_1 \cdot VM_0 \cdot (1 - B_3) \cdot (1 - \exp[-A \cdot t \cdot \exp(-B_2/T)]) \qquad (1)$$

The devolatilization curves show that devolatilization starts about 20 msec after the injection, i.e. approximately at the end of the heat-up period. The time scale used in the equation therefore starts 20 msec after injection. This indicates that the devolatilization during the heat-up period is only very small, and that the devolatilization occurs essentially at a constant temperature.

As Badzioch and Hawksley pointed out, the experimental conditions were chosen such that it might be safely assumed that only primary decomposition took place and that no secondary degradation of the tars occured. This was mainly achieved by the short residence times, the high sweep gas-to-coal mass flow ratio, and the small particles. Additional experiments with larger particles (up to 60 μm) showed no effect of the particle size on the devolatilization. This indicates that the heat and mass transport processes are not rate controlling for these experimantel conditions.

Despite the complexity of the processes during the heat-up period (mixing and heat conduction), we assumed in our modeling constant heating rates for each case. However, in order to reach the final temperature after 20 msec, the heating rate had to be adjusted to each final temperature.

Unfortunately, the theoretical results obtained by the proposed mechanism could not be compared directly with the experimental points of coal D, the one we had selected, since in ref. [11] only the experimental points for a coal B are reported. Therefore the comparison will be made between the curve we calculated using equation 1 with the empirical values given for coal D, and the theoretical results obtained with our own kinetic scheme.

C Work done by Peters and Juentgen at the Bergbauforschung GmbH, Germany (BBF)

Peters, Juentgen, and colleagues approached the problem of coal pyrolysis kinetics from two sides. First, they formulated a kinetic theory for non-isothermal experiments with thermal degradation reaction, where the temperature increases linearly with time [30,31,32]. They made some parametric studies to determine the changes in the gas release rate as a function of temperature, if the activation energy, the frequency factor, the heating rate or the final temperature are varied. They derived a very useful expression [32] that correlates the heating rate m and the temperature T_m at which maximum gas release occured:

$$\ln\left[\left(\frac{m}{T_m^2}\right)\left(\frac{E}{RA}\right)\right] = -\frac{E}{RT_m} \qquad (2)$$

This equation, which was derived for a first-order, Arrhenius type rate law, gives a linear relation between $\ln(m/T_m^2)$ and $1/T_m$, if the reaction mechanism remains the same over a certain range of heating rates.

The structure of coal is very irregular, and the bonds that have to be broken to release volatile matter do not have the same bond energies because they are differently influenced by the surrounding atoms. This influences the activation energies which are closely coupled with the bond energies. Therefore, the concept of reaction complexes was introduced, where a certain distribution of activation energies and frequency factors is used to describe the rate of a reaction [2]. This model has been used successfully also by other investigators [26,33].

In the experimental work done at BBF [2,21] the gas release rate of hydrocarbons (CH_4 up to C_3) was measured for various heating rates (10^{-4} to 10^{+3} C/sec) for different coals. For the comparison with our model the results for the coal Fuerst Leopold, a hvAb coal, was used.

The main results can be summarized as follows:

A) For all hydrocarbons a linear relation between $\ln(m/T_m^2)$ and $1/T_m$ was found over the whole range of heating rates that was investigated. This led to the conclusion that the mechanism for the production of these species does not change for these heating rates and temperatures.

B) The best fit of the experimental yield versus temperature curves for the higher hydrocarbons (C_2 and up) was obtained by using a rate law with a distributed activation energy and frequency factor (reaction complex). It was also possible to obtain kinetic values for the case of a single reaction (discrete activation energy), but there the agreement between the experimental and the theoretical curves was not as good as for a reaction complex.

Besides these two major works done at BCURA and BBF, information from other publications has been used to obtain a better picture of the process and to justify certain numbers or certain relations between different parameters (see sections 4 and 9).

3. General Scheme For Coal Pyrolysis

The reaction scheme which we want to propose should be applicable over a wide range of parameters, representing if possible all important parameters in real commercial systems. Following are some of the observed trends which should be reflected in such a model.

1.) Yields of volatile matter increase with increased final temperature of the process [26,27,16],

2.) Yields of volatile matter increase with increasing heating rates [10,11,12,16],

3.) Slow heating rates (carbonization processes) yield less tar than fast devolatilization processes,

4.) Increasing bed height in a fixed bed reactor decreases the yield of volatile matter [4,28],

5.) Tar vapors can be cracked at temperatures above 600 C

[14,15,29,27,30],

6.) Increasing particle size decreases the tar yield,

7.) The yield of the various classes of products vary with pressure in the reactor, in ways that depend on the type.

It is possible that items (4) and (6) are, in part, related to items (1),(2), and (3), but there may be additional factors not encompassed by the earlier noted trends, which cause these macroscopic trends. The effects (4),(6), and (7) are a result of the interplay between chemical kinetics, heat and mass transport processes, and fluid flow processes. In the BCURA and BBF works, these effects were minimized in the design of the pyrolysis experiments, in order to bring out particularly the purely chemical-kinetic results, (1),(2),(3), and (5).

Our first attempts have been directed toward simulating most of the above noted trends or characteristics. The reactions will be formulated in terms of generalized compounds, similar to van Krevelen's scheme, which did not attempt to specify the chemical constituents of each type of product.

Based on these findings and various weight loss curves reported in the literature, a general kinetic scheme for coal pyrolysis can be postulated (Table II). Even this scheme, more elaborate than that of van Krevelen, can only be a very simplified picture of the real process, due to the limited number of reactions and of classes of products and reactants.

This scheme can be divided into five main parts:

1.) Activation step (reaction 1) : The coal molecule is activated, bond scissions will occur, and radicals and smaller fragments of the original coal structure are produced.

2.) Primary decomposition (reactions 2 - 5) : the activated coal undergoes further reactions (additional bond breaking, radical recombination reactions, etc.) to form the primary volatile matter (primary tar and primary gas).

3.) Deactivation step (reaction 6) : At low temperatures, where the primary decomposition reactions are still very slow, part of the activated coal may deactivate again. This deactivation will probably not be simply the reverse reaction to the activation step, since it is very unlikely that, once the complex coal structure is broken up, the fragments will recombine to exactly the same structure. Probably the deactivated coal will have a more stable structure than the original coal.

4.) Reaction 7 and reaction 8 : the liquid primary tar has two routes to go. If sufficient heat is supplied it can vaporize (inside the particle or at the surface). If, however, the heat flux, i.e. the vaporization rate, is very slow, then the liquid primary tar (which is not a very stable molecule) can follow the competing reaction 7 and polymerize inside the particle. This polymerization will probably yield some secondary gas as well as augment the char.

5.) Gas phase degradation (reaction 9 and 10) : that portion of the tar that has vaporized and diffused out through the coal pores, can undergo secondary decompositon reaction in the hot reactor, until it is swept out and quenched. These reactions are probably catalyzed at the surface of the coal particles. This degradation can be divided into two reactions: reaction 9 describes the polymerisation in the gas phase and reaction 10 the cracking of the primary tar.

The gas phase degradation reactions 9 and 10 from primary tar to just a secondary gas and a solid residue, are certainly very simplified. Some of the tar will actually degrade to a liquid secondary product (i.e. light oils), and surely the primary gas can be cracked further. At present it does not seem reasonable to add more complexity to the degradation, since it is very difficult to divide experimental results into effects due to the primary decompostion and into effects due to the secondary degradation.

This general scheme , however, had to be simpilfied in order to assign kinetic values to the different reactions, because of the limited experimental data. Therefore the following simplifications were introduced:

- Very small particles (i.e. physical processes like heat and mass diffusion are not rate controlling, because the characteristic diffusion time is small).
- Uniform temperature throughout the particle
- Instantaneous vaporization (i.e. no decomposition in the liquid phase).
- Time for deactivation negligible.

This means that the heat transfer and mass diffusion processes are set aside in the fitting of our model to the available data. These simplifications will, of course, limit the applicability of the reduced kinetic scheme to cases involving small particles.

The last assumption had to be made for the following reasons: The deactivation occurs mainly in low temperature processes. In these processes, the degradation of the liquid tars will also be appreciable, because the vaporization rate will be slow. Both reactions occur inside the particle and decrease the yield of volatile matter. There are no experimental data available that would indicate how much of the decrease in volatile matter yield is due to any of these two reactions. Therefore, if we neglect the liquid tar polymerization we will also have to be consistent and neglect the deactivation.

The above assumptions lead to the simplified scheme shown in Table III. This scheme consists of three parts:

a) activation step

b) primary decomposition to gaseous primary tar and primary gas (reactions 2 - 5).

c) secondary degradation of the primary tar in the gas phase (reactions 6 - 7).

In the remainder of the text the term primary decomposition generally will include the activation step.

4. Primary Decomposition

The main part of this paper will be concerned with the primary decomposition (i.e. reactions 1 - 5 of the simplified scheme, Table III). For this part of the scheme numerical values for the kinetic parameters have been obtained by fitting the theoretical curves to the data reported in the literature cited above. In the BCURA and BBF tests, the degradation of the released volatiles was presumably negligible, so reactions 6 and 7 played little role. First, however, the reasoning that led to each of the reactions 1 to 5 will be briefly summarized.

These five reactions form a model for the primary decomposition of coal. The initial activation step is followed by two parallel sequences for the decomposition of the activated coal: a low activation energy sequence, consisting of reactions 2 and 4, which will be favored at low temperatures, and a high activation energy sequence (reactions 3 and 5) for high temperature processes.

Reaction 1 :

At the beginning of our work, several different reaction schemes had been formulated that consisted of several decomposition reactions (similar to reactions 2 - 5), but without the activation step. The kinetic numbers had been selected to fit the BCURA results [11]. However, it was found that these schemes could not be applied to slow carbonization processes with heating rates of 10^{-2} C/sec and slower, because in the theoretical predictions of these slow processes the coal would then decompose between 100 C and 200 C. That is, the reaction rates of the low activation energy decomposition reactions, adjusted to the fast processes, turn out to be much too fast at these low temperatures.

Therefore the activation step with a high activation energy was introduced. This reaction, interpreted as bond-breaking, provides an energy barrier for processes at low and medium temperatures, while it is no longer rate controlling at high temperatures.

Reaction 2 and 3 :

After the raw coal is converted to " activated coal " , it can undergo two different reactions, depending on the temperature. One is a low activation energy reaction forming tar (reaction 2), and the other is a higher activation energy reaction forming primary gas. These two reactions also produce intermediate solids, S_1 and S_2 , respectively. They had to be introduced because it was found by many investigators that the ratio of gas/tar yields increases with increasing temperature. The tar forming reaction must have the lowest activation energy of all reactions, since throughout the literature the tar is reported to be driven off first in a pyrolysis process.

Reaction 4 :

Many slow carbonization experiments [2,4,19] report gas evolution up to high temperatures (600 C - 800 C), which means that this gas producing reaction must have a high activation energy. Since it is very likely that for these processes all activated coal follows reaction 2 , we have to provide a succeeding reaction of the intermediate solid S_1 to produce primary gas. As suggested by Juentgen [2] in connection with the formation of CH_4 , this gas formation may result from several reactions. But in order to keep the mathematical approach tractable, we have introduced only reaction 4 in addition to reaction 2 in the low temperature sequence. Limiting the primary decomposition scheme at low temperatures in this way to only one gas forming reaction (reaction 4) cuts off the gas evolution at lower temperatures than observed. This is a minor defect in the model at this time which can be remedied if desired.

Reaction 5 :

Badzioch and Hawksley [11] found that even at 950 C some volatile matter is left in the coal after 100 msec which can be driven off the coal by a comparatively long-duration proximate analysis. This volatile matter remained in the coal even when the weight loss curve measured in the high tmeperature experiment showed a clear levelling off after about 40 msec. Kimber and Gray [13] on the other hand found that no volatile matter is left in the coke after the same time period, when the decomposition temperature was 1800 C. This indicates that there is another high activation energy reaction that produces gas from an intermediate solid. This is modelled by reaction 5 .

5. Mathematical Description and Numerical Scheme

In order to formulate the differential equations that describe the decomposition as a function of time, we have to define the orders of the different reactions. In general, it would have been possible to formulate the equations with unknown reaction orders, but this would have added emormous complexity to the equations and to the numerical scheme to solve them. Fortunately, there are indications in the literature that can be used to select the reaction orders in advance.

Wiser et al. [19] observed a changing reaction order for low temperature experiments (400. C - 500. C), from second order at the beginning to zero order at the end of the experiment. On the other hand, many investigators suggested first order laws. Badzioch and Hawksley [11] obtained a very good fit of their high temperature experiments with a single first order equation. Peters and Juentgen [2,21], Pitt [5], Anthony [26], and Bennhack [33] also used first order expressions. They introduced " reaction complexes " with a distributed activation energy and frequency factor.

In this reaction scheme we did not use distributed activation energies, in order to keep the mathematical procedure simple. However, it might be worthwhile to incorporate the reaction complexes later for two reasons :

1.) Good agreement between experimental and theoretical curves has been obtained by this method [22].

2.) The irregular coal structure suggests strongly the model of a reaction complex.

Since in our theoretical model the process at slow heating rates and/or low temperatures (< 600 C) is controlled by the activation step, this reaction was chosen to be of second order, based on the findings of Wiser et.al. The other reactions are assumed to be of first order, following the data reported for the fast processes. These assumptions about the order of the reactions lead to the following system of nonlinear ordinary differential equations for the primary decomposition:

$$
\begin{aligned}
dC/dt &= -k_1 \cdot C^2 \\
dAC/dt &= k_1 C^2 - (k_2 + k_3)\, AC \\
dPT/dt &= x_2\, k_2\, AC \\
dPG/dt &= x_3\, k_3\, AC + x_4\, k_4\, S_1 + x_5\, k_5\, S_2 \\
dS_1/dt &= (1 - x_2)\, k_2\, AC - k_4\, S_1 \\
dS_2/dt &= (1 - x_3)\, k_3\, AC - k_5\, S_2 \\
dS_3/dt &= (1 - x_4)\, k_4\, S_1 \\
dS_4/dt &= (1 - x_5)\, k_5\, S_2
\end{aligned}
\qquad (3)
$$

Since reaction 1 is a second order reaction the system is nonlinear. Therefore, even for a constant temperature process, this system cannot be solved algebraically in closed form. A step-wise finite difference scheme was selected to solve the system numerically for a given temperature-time curve. The scheme is an implicit integration method that has been developed specifically for chemical kinetic problems (i.e. stiff differential equations) [34]. The integration method is of second order. The error in each time step is calculated using the neglected third order term. This error is then used to control the step size. A detailed description of the numerical scheme is given in [34].

6. Selection of the Kinetic Parameters

A Stoichiometric Coefficients

Since all the primary decomposition reactions have a solid as the reactant, the structure and molecular weight of which are unknown, the stoichiometric coefficients are defined as mass stoichiometric coefficients.

The maximum possible tar yield is given by x_2 . If all coal follows the low temperature route (up to about 700 C) then x_2 is equal to the yield of primary tar. For most of the fast processes (e.g. fluidized beds) tar yields of between 20 % and 30 % are reported. But recently Sass [37] and Kentser et.al. [35,36] reported yields of up to 36 % and 40 %, respectively. Therefore x_2 was chosen as 0.4.

Badzioch and Hawksley measured an overall weight loss of 49 %. This indicates that the low temperature gas forming reaction must yield 9 % gas, which corresponds to x_4 =0.15. This is supported by Kentser [35] who found a gas yield of 9 % at 700 C (together with 40 % tar).

The high temperature route consists of reactions 3 and 5. Since under the fast BCURA conditions, reaction 5 does not contribtue any gas, reaction 3 must have a gas yield of approximately 50 %, i.e. x_3 =0.5.

The highest volatile matter yields to date have been reported by Kimber and Gray [13] and Stickler [25]. Both found a maximum of about 72 % for very fast (10^5 C/sec) and very high temperature (2000 - 2500 C) experiments. If we assume, that at these temperatures and heating rates all coal decomposes via the high temperature route, then the stoichiometric coefficient for reaction 5 must be x_5 = 0.4, in order to yield 70 % volatile matter.

B Activation Energies and Frequency Factors

Reaction 1 :

This reaction is the activation step, which prevents the coal from decomposing at low temperatures in a slow heating process. The reaction is of second order, hence the rate law has the following form (equation 3):

$$dC/dt = -k_1 C^2 = -A_1 \exp(-E_1/RT) \cdot C^2$$

When the rate constants were determined, reaction 1 was still considered to be of first order. But the principal reasoning for obtaining the kinetic values does not change if we go to a second order expression. Therefore the derivation of the numbers using a first order rate law will be presented here. The numerical results show that the change in reaction order did not require a change of the kinetic values.

The reason for starting with a system of first order reactions was to simplify the mathematical procedure. The system of ordinary differential equations, that describe the changes in concentrations for such a reaction scheme, is linear and therefore can be solved analytically for a constant temperature. This then has a big advantage in terms of computing time and accuracy of the numerical results.

As mentioned earlier, reaction 1 has to satisfy two conditions:
A) Serve as an energy barrier to prevent early decomposition (at temperatures < 200 C) for slow processes. (BBF data [2,21] was usdd to check this).
B) High reaction rates at temperatures above 650 C, to allow fast processes like the BCURA experiments.

Using basic kinetic principals, Peters et.al. [38] derived a formula for the gas release of a thermal degradation reaction (for constant heating rate and a first order rate law) . This relation can be written in terms of the decomposition rate of the undecomposed coal C :

$$\frac{C}{C_o} = exp\left[-\frac{A}{m}\cdot\frac{RT^2}{E}\cdot e^{-\frac{E}{RT}}\right] \quad \left(= \frac{V_o - V}{V_o}\right) \qquad (4)$$

where the term C/C_o is equivalent to the term $(V_o - V)/V_o$ that has been used by Peters to characterize the degree of decomposition.

From the BBF results we obtain the following characteristic temperatures [2]:

$m = 4.2\cdot10^{-4}$ C/sec	$T_m = 360.$ C
$m = 4.3\cdot10^{-3}$ C/sec	$T_m = 400.$ C
$m = 1.5\cdot10^{-2}$ C/sec	$T_m = 430.$ C

where T_m is the temperature at which the maximum gas release rate is measured (this occures when about 50 % or more coal is decomposed). This implies that at $T = T_m$ about 30 % to 50 % of the coal should be decomposed.

The second condition implies, that the activation should be essentially complete after the heat-up period of 20 msec. This gives $C/C_o \approx 0.05$ for m = 35000. - 50000. C/sec after t = 20 msec

Using equation 4, we can now calculate the value for C/C_o for these different heating rates using several pairs of A_1 and E_1 and then select those values that promise the best fit. The results are shown in Table IV.

The values for C/C_o for $m = 4.3\cdot10^{-3}$ C/sec are always somewhat lower than they should be, or than the values for $m = 4.2\cdot10^{-4}$ C/sec or $1.5\cdot10^{-2}$ C/sec. This is because the temperature, T_m, cannot be determined exactly enough from the graphs in [2]. A small corretion in T_m (decrease) would bring the results into the right range.

The results for E_1 = 70 kcal/mole show that the decomposition at the high temperatures is too slow, while for E_1 = 80 kcal/mole the energy barrier is too high for the slow heating processes. Therefore a value of E_1 = 75 kcal/mole has been selected and the corresponding frequency factor has been determined to satisfy the two conditions.

The slow decomposition results should not change appreciably when we assume a second order rate law for the activation step, because only that part of the process in which the coal mass fraction is greater than 0.5 was considered. The major difference in the behavior of a second order reaction compared to a first order reaction occur, however, when the mass fractions are small (< 0.25). For the high temperature process, the difference resulting from a first order and a second order rate law is shown in Figure 2. It shows the decrease of the coal mass fraction for two temperatures (973 K, 1223. K). This figure indicates very clearly that for T=973. K a small difference in the degree or conversion at 20 msec is expected, while for T = 1223 K, even with the second order reaction, all coal is converted well before t = 20 msec.

Therefore, the two conditions that were used to derive the kinetic values for the activation step are also satisfied with a second order reaction, without any change in the kinetic values themselves.

Reaction 2 and 3 :

The reaction rates of the reactions 2 and 3 are based only on the BCURA results, because these are the only data, for which secondary degradation is insignificant. These data also have one big disadvantage, however, because only the overall volatile matter loss is reported and no distinction between tar and gas is made.

To obtain kinetic values, the initial slopes of several BCURA curves (at different temperatures) were used. The initial production rate of BCURA is :

$$dW/dt = D \cdot A \cdot \exp(-B_1/T) \qquad (5)$$

Using the appropriate empirical constants for coal D (given in [11]), we obtain for the different temperatures:

T (K)	973	1023	1073	1123	1173	1223
dW/dt (sec^{-1})	7.02	10.98	16.47	23.83	33.41	45.56

This initial weight loss of BCURA will be set equal to the weight loss predicted by our reaction scheme at 20 msec. If we assume that at 20 msec the decomposition just starts, then no solids S_1 and S_2 have formed yet and the reactions 4 and 5 do not contribute to the weight loss. Therefore the " initial " weight loss can be approximated as follows :

$$dW/dt = x_2 \ k_2 \ AC^* + x_3 \ k_3 \ AC^* \qquad (6)$$

where AC^* is the mass fraction of activated coal at t = 20 msec, which is determined from the activation reaction at 20 msec. These values can be obtained using equation 4 together with the different heating rates and final temperatures, resulting in :

T (K)	973	1023	1073 . . . 1223
AC	.84	1.00	1.00 . . . 1.00

If it is assumed that for T = 973 K and T = 1023 K all coal converts through reaction 2, the activation energy and the frequency factor of reaction 2 can be calculated using equation 6. This gives

$$A_2 = 5501. \ sec^{-1}$$
$$E_2 = 10.768 \ kcal/mole$$

To obtain the kinetic values for reaction 3, the initial weight loss at T = 1123 K and T = 1223 K is matched with the analytic expression. At these temperatures both reactions (reaction 2 and 3) contribute. This calculation then leads to

$$A_3 = 3.4 \cdot 10^6 \ sec^{-1}$$
$$E_3 = 31.06 \ kcal/mole$$

These values however, result in too high a reaction rate at T = 973. K. To reduce the reaction rate at T = 973 K, and to simultaneously keep the rates high at T = 1100 - 1200 K, the activation energy E_3 had to be increased. Small changes in the frequency factor A_2 also improved the fit. Finally the best results were obtained for

$$A_2 = 4.5 \cdot 10^3 \ sec^{-1} \qquad A_3 = 3 \cdot 10^8 \ sec^{-1}$$
$$E_2 = 10.7 \ kcal/mole \qquad E_3 = 40. \ kcal/mole$$

All this was done for a first order activation step. The introduction of a second order activation step did change the results only by about 1/2 %, which is well within the limits of the accuracy of the BCURA data.

The big uncertainty in these values however is the assumption that at T = 973 K and 1023 K all activated coal decomposes via the low temperature route. Since Badzioch and Hawksley did not report any tar or gas yields, this assumption cannot be verified at the moment. Other yield curves indicate that the maximum tar yield is reached between 600 - 700 C [27,35]. But in these experiments secondary decomposition cannot be excluded. However, it will be shown that by choosing another set of kinetic values for reactions 2 and 3, the overall BCURA curves and different tar/gas ratios can be predicted.

In order to increase the gas yield and decrease the tar yield, both activation energies had to be lowered. An activation energy, E_2 = 5 kcal/mole, was arbitrarily chosen and the other values were determined again by matching the intial slopes. No real optimization was carried out, but the fit with the BCURA curves was reasonably good for

$$E_2 = 5.\ \text{kcal/mole} \qquad E_3 = 30.\ \text{kcal/mole}$$

Figure 3 shows the tar and gas yields as a function of temperature for a devolatilization process of 100 msec duration. It is now clear from this figure, that the primary decomposition scheme can easily be adjusted (if necessary) to new experimental data which reports the primary tar and the primary gas yields separately.

Reaction 4 :

Modeling the slow heating process of BBF means that all activated coal decomposes via reactions 2 and 4 . Therefore, the only gas forming reation is reaction 4 and the results of Peters and Juentgen for the gas production have to be matched by reaction 4 . As mentioned earlier, it will probably not be possible to fit the whole shape of the gas release curve, but the changes of the temperature T_m with changing heating rates can be simulated. Figure 4 shows the results for

$$A_4 = 1.7 \cdot 10^{13}\ \text{sec}^{-1}$$
$$E_4 = 55.\ \text{kcal/mole}$$

and the comparison with the BBF curves. Figure 5 shows the influence of the kinetic values for reation 4 on the relation between the temperature T_m and the heating rate m. The corresponding pairs of A_4 and E_4 have been selected to obtain a good fit with the BCURA curves.

Reaction 5 :

The kinetic values for this reaction have been chosen rather arbitrarily. Due to the scacity of experimental data for high temperature (> 1300 K), short duration processes (Kimber and Gray only reported about ten experimental points at different temperatures), no detailed analysis of the influence of this reaction has been made.

The activation energy of 55 kcal/mole was chosen arbitrarily and the frequency factor determined, so that at the experimental conditions of Badzioch and Hawksley no appreciable degradation of S_2 to S_4 took place. This was necessary to explain the residual volatile matter found in their experiments.

7. Agreement With the Experimental Data

The following numbers for the stoichiometric coefficients, the activation energies, and the frequency factors have been found to give the best agreement with the experimental data:

Reaction	x	A (sec^{-1})	E (kcal/mole)
1	1.0	$2.0 \cdot 10^{20}$	75.
2	0.4	$4.5 \cdot 10^{3}$	10.7
3	0.5	$3.0 \cdot 10^{8}$	40.
4	0.15	$1.7 \cdot 10^{13}$	55.
5	0.4	$1.0 \cdot 10^{10}$	55.

A Comparison With BCURA Results

Figure 6 give a comparison between the theoretical BCURA volatile matter yield curves and the predicted curves obtained from the primary decomposition scheme for six different temperatures.

By fitting their results with one single rate expression, Badzioch and Hawksley [11] assumed that no appreciable decomposition had taken place during the heat-up period. They found the heat-up time to be about 20 msec. Only after this 20 msec, the decomposition proceeds at a constant temperature, which they use in their rate expression. The starting point for the decomposition was determined by extrapolating the curve through the actually measured points to the line where the weight loss was zero. The data points were taken only at t = 30 msec and later. This exprapolation, however, might not represent the true devolatilization curve at these early times.

With the proposed mechanism the heat-up period must be included because of the activation step (reaction 1) which is fast at temperatures above 600 C. Therefore the results obtained by our scheme already show some decomposition in the first 20 msec, depending on the temperature. This probably is a better representation of the true devolatilization curves than the BCURA curves.

The curves show a very good agreement for t > 30 msec and the differences between the present predictions and the BCURA curves are not more than 1.5 %. This is certainly less than the error between the empirical BCURA curves and the actual data points, as obtained in the experiment.

Figures 7 and 8 give an indication of the concentration variations versus time for the different compounds and two different temperatures. The rapid decrease of the C mass fraction and the corresponding increase in AC should be noted. This shows that under these rapid heating, high temperature conditions the activation step is not rate controlling, but goes to completion during the heat-up period.

B Comparison With PBT Results

Peters and Juentgen [21] found, that their experimental results for a heating rate range of 10^{-4} C/sec to 10^{+3} C/sec gave a straight line for each hydrocarbon species. The curves for methane and ethane were used for comparison with our kinetic scheme, since all the other curves lie between these two. The results are shown in Figure 4. The heating rates that are covered in this graph are $m = 10^{-4}$ C/sec at $1/T_m = 1.5 \cdot 10^{-3}\ K^{-1}$ and $m = 10^{3}$ C/sec for $1/T_m = 10^{-3}\ K^{-1}$. The corresponding temperatures are 393.C and 727.C, respectively.

C Some Comments About The Reaction Constants

Figure 9 shows the reaction constants for the five reactions versus 1/T (Arrhenius plot). The following characteristics can be observed.

Reaction 1 is rate controlling up to about 800 K. Up to this temperature, all activated coal is immediately converted to primary tar and the intermediate solid S_1 , since, (a) reaction 2 is much faster than reaction 1 , and (b) reaction 3 (which is the second possibility for the decomposition of activated coal) is even slower than reaction 1 . Above 850 K, activated coal is accumulated, since the succeeding reactions are slower than the activation step. Comparison of the two parallel reactions 2 and 3, that follow the activation step shows that the tar formation is favored up to temperatures of 1300 K, at which temperature the reaction rates are approximately equal. Up to around 1000 K reaction 4 is slower than the preceeding reaction 2, therefore an accumulation of solid S_1 occurs. This will result in the gas release occurring after the tar release, which is observed in all devolatilization experiments. The rates of reaction 3 and 5 are equal at about 2000 K .

8. Chemical Interpretation of the Activation Step

The mechanism and rate of coal pyrolysis depend, of course, on the molecular structure of coal. Coal is a polymeric compound (or perhaps a mixture of such compounds) containing polynuclear aromatic, aliphatic, and some heterocyclic groups. While there is some disagreement about the precise structure (for example the number and length of the aliphatic chains that sometimes link aromatic and acyclic systems [39,40,41]) some general features can be agreed upon. In particular it seems that coal contains a polymeric molecule (or molecules) having C-C, C-H, C-S, C-N, C-O,OH, and NH bonds (in varying degree of saturation), but that there are no unstable three or four member ring structures.

Some conclusions about the mechanism of the activation step can be drawn from this limited information. First, in order to form a low molecular weight hydrocarbon fraction, carbon-carbon bonds must be broken at some point in the mechanism. This fact is consistent with the high activation energy proposed for the activation step. The activation energy for simple C-C bond scission must be of the order of the bond energy, which is about 85 kcal/mole (for C_2H_6 it is 85 kcal/mole ; for $C_4H_{10} \longrightarrow 2\ C_2H_5$, it is 82 kcal/mole) [42]. For elimination of ethylene in simultaneous rupture of two carbon-carbon bonds, activation energies of 65 kcal/mole are typical for six-membered ring systems.

It was shown that the only acceptable value for the pre-exponential factor for the rate constant was $2 \cdot 10^{20}\ sec^{-1}$, wheras the largest measured frequency factors for bond scissions are of the order of $10^{17.5}\ sec^{-1}$ [42]. However for the degradation of polytetrafluoroethylene (teflon) a frequency factor of about $10^{19}\ sec^{-1}$ was measured [43] and a complex radical mechanism in the solid phase was proposed for this process. Therefore, the activation step may involve not a single elementary reaction, but a complex radical mechanism with chain reactions, such as the following example

$$R{-}CH_2{-}R' \longrightarrow R\cdot' + CH_2{-}R\cdot$$
$$R\cdot' + R''H \longrightarrow R''\cdot + R'H$$
$$R\cdot'' \longrightarrow AC + R\cdot'$$

where R , R' , R'' denote functional groups in the coal structure. A similar mechanism has been proposed by Wiser et.al. [19].

9. Secondary Decomposition

It is much more difficult to obtain and interpret experimental data about the secondary decomposition than it is for the primary decomposition, because the effects of the secondary degradation are always coupled and/or covered by the effects of the primary decomposition. But there is some, mostly qualitative, information available that can be used to support a secondary decomposition model consisting of two gas phase reactions.

Peters [22] investigated the differences between the tars from a low temperature carbonization and from a high temperature, fast pyrolysis. He cracked the high temperature tars and found that the cracking products were substantially different from the low temperature tars. Since a low temperature carbonization is a very slow process, the volatile matter that is driven off here is to a large extent the product of a secondary degradation. The difference in the products from a slow process and the cracking products of high temperature tar then indicates that there must be two different degradation reactions. Therefore, the two reactions 6 and 7 of the simplified scheme have been formulated:

$$PT \longrightarrow x_6\ SG_1 + y_6\ S_5$$

$$PT \longrightarrow x_7\ SG_2 + y_7\ S_6$$

The polymerization is a low activation energy reaction, while the cracking occurs at high temperatures (> 600 C), i.e. it has a high activation energy.

Some data has been reported in the literature that can be interpreted as the result of gas phase polymerization. Mazumdar [4] and Essenhigh et.al. [28] found a relationship between the depth of a fixed coal bed and the coke and volatile matter yields, respectively. Mazumdar used a slow heating process (Gray King Assay) while Essenhigh et.al. used heating rates between 16 C/sec and 20 C/sec. With increasing bed depth the coke yield increased, while the volatile matter yield decreased. Mazumdar found no evidence of any cracking reactions. Therefore the only explanation for those curves is the polymerization reaction in the gas phase. The deeper the bed, the longer the residence time of those vapors that originate from the lower levels, while the vapors from the top layers of the bed still can escape relatively unaltered. Mazumdar reports a decrease in tar yields from 15 % at " zero bed thickness " to 3 % in large coke ovens. This was accompanied by an increase of coke yield from 71.5 % up to about 78 % . This indicates that the polymerization degrades the tar to a solid and a gas (or light oil).

Not much data is reported in the literature on the cracking of the primary tars. However, at least one observation has been made by several investigators [14,15,27,29,30]: there is no appreciable cracking of tar vapors at temperatures below 600 C . In the normal temperature range of coal pyrolysis processes (< 1000 C) the gaseous hydrocarbons will not crack . Therefore we will only consider the thermal cracking of the primary tars.

In order to consider the secondary degradation reactions in our model, we have to formulate a mathematical model of the gas flow through the reactor. This is necessary to determine the residence time of the volatile matter that is released from the solid in the reactor.

Our present approach is directed towards the formulation of a very simple model to simulate the fixed-bed conditions that have been used by Essenhigh et.al. and Mazumdar to obtain their curves of volatile matter (or coke) yield as a function of the bed height. These two curves will be used to select the kinetic parameters for reactions 6 and 7.

The following simplifying assumptions have been made to formulate a mathematical model of the fixed bed reactor:

- no change in porosity (i.e. void space) during the decomposition of the coal particle
- no pressure drop (p = const.)
- specified temperature history (constant over x)
- constant cross section
- uniform distribution of the coal in the bed, hence constant gas

and tar release rates over x

- temperature in the gas phase is equal to the uniform particle temperature
- diffusion in the gas phase can be neglected in comparison with the convective transport

This implies that the momentum and energy equation do not have to be utilized and only the conservation equations for mass and species need to be solved.

The gas and the tar production rates are calculated independently using the primary decomposition scheme and the given temperature-time curve. This separation is possible, because the primary degradation is not influenced by the secondary degradation.

The stoichiometric coefficients x and x for the two gas phase reactions are defined on a molar basis. Therefore, molecular weights have to estimated for the gaseous species. The coefficients y and y for the production of solid material are defined as the number of grams of solid produced by the degradation of one mole of primary tar. It is not necessary to know the number of moles of solid (which would depend on the unknown molecular weight), since the material balance is not based on molar quantities.

For the non-steady gas flow through the bed the following conservation equations can be derived:

Mass Continuity

$$\frac{\partial \rho}{\partial t} + u \frac{\partial \rho}{\partial x} + \rho \frac{\partial u}{\partial x} = \frac{1}{y} (PR_T + PR_G) + RR_{Solid} \qquad (7)$$

Species Continuity

$$Y_i \frac{\partial \rho}{\partial t} + \rho \frac{\partial Y_i}{\partial t} + Y_i \rho \frac{\partial u}{\partial x} + Y_i u \frac{\partial \rho}{\partial x} + \rho u \frac{\partial Y_i}{\partial x} = \frac{1}{y} PR_i + RR_i \qquad (8)$$

Four species are present in the gas phase: primary tar, primary gas, secondary gas, and carrier gas (sweep gas). The carrier gas may be the fluidizing gas in a fluidized bed reactor or the transport gas in a transport reactor. It will be treated as an inert gas that only dilutes the volatiles and sweeps them out of the reactor.

The reaction rates that correspond to the two gas phase reactions, 6 and 7 are:

$$RR_{PT} = -(k_6 + k_7)\ Y_{PT}$$

$$RR_{SG} = (x_6 k_6 + x_7 k_7)\ Y_{PT}\ (M_{SG}/M_{PT})$$

$$RR_{Solid} = -(y_6 k_6 + y_7 k_7)\ Y_{PT}\ (1/M_{PT})$$

$$RR_{PG} = RR_{CG} = 0.$$

Using equation 7, equation 8 reduces to the following system of coupled, non-linear partial differential equations :

$$\frac{\partial Y_i}{\partial t} + u\,\frac{\partial Y_i}{\partial x} = \frac{1}{\rho}\left\{\frac{1}{\nu}\,PR_i + RR_i - Y_i\left(\frac{1}{\nu}\left[PR_T + PR_G\right] + RR_{Solid}\right)\right\} \qquad (9)$$

with $Y_i = Y_{PT},\ Y_{PG},\ Y_{SG},\ Y_{CG}$

Under the assumption, that all gas phase components follow the ideal gas law, the following is true

$$\rho = \frac{P}{RT}\left(1 \Big/ \sum_{j=1}^{4} \frac{Y_j}{M_j}\right) \qquad (10)$$

and with this equation of state the partial derivatives $\partial\rho/\partial t$ and $\partial\rho/\partial x$ in equation 7 can be eliminated and after some rearrangements an ordinary differential equation to to calculate the velocity can be obtained:

$$\frac{du}{dx} = \frac{RT}{P\nu}\left(\frac{PR_T}{M_{PT}} + \frac{PR_G}{M_{PG}}\right) + \left\{(x_6 - 1)k_6 + (x_7 - 1)k_7\right\}\frac{Y_{PT}}{M_{PT}\sum_{j=1}^{4}\frac{Y_j}{M_j}} + \frac{1}{T}\left(u\frac{\partial T}{\partial x} + \frac{\partial T}{\partial t}\right) \qquad (11)$$

The system of partial differential equations will be solved numerically using a linear finite element method with a generalized implicit time marching procedure. The non-linear inhomogeneous terms will be quasilinearized using the first term of a Taylor-series expansion.

Kinetic values for the two degradation reactions will then be selected in order to obtain good agreement between the theoretical yields for different bed heights and and the experimental data.

10. Summary and Conclusions

A kinetic model for coal pyrolysis has been developed that can be used for the theoretical optimization of coal conversion processes. In contrast to many previously proposed schemes, this model has been formulated in terms of general compounds like tars, gases, and solids, i.e. the volatile matter has been divided into liquid and gaseous products. Furthermore, a high activation energy step has been introduced to convert the raw coal to activated coal. With this activation step it is possible to apply the scheme over a wide range of temperatures and heating rates, unlike other schemes that have been limited to narrow ranges.

The proposed kinetic model consists an activation step, four primary decomposition reactions in the solid phase, and two degradation reactions in the gas phase. Good agreement between previously published experimental results and the theoretical predictions for primary decomposition has been obtained over a wide range of heating rates (10^{-4} to 10^{+5} C/sec) and, associated with it, over a wide range of temperatures (400 C to 950 C).

The kinetic model has been formulated and the kinetic parameters have been obtained for a high volatile A bituminous coal. However, with appropriate new numerical values for the stoichiometric coefficients, the activation energies, and the frequency factors, the scheme should also be applicable for coals of different ranks. An exception may be anthracite, because of its very low volatility. Following the procedure used for the hvAb coal, these new kinetic constants could be determined, especially since Badzioch and Hawksley as well as Peters and Juentgen did repeat their experiments for several coals of different ranks.

If kinetic parameters were available for different coals, these parameters probably could be correlated with some characteristic properties of the coal, e.g. the ultimate or the petrographic analysis. In this way the scheme would then become more broadly applicable for different coal ranks.

The work that has been done so far is only the first step towards a theoretical technique for optimizing coal conversion processes. However, the scheme gives a deeper understanding of the pyrolysis process and opens many options for additional work and applications.

A refinement of the scheme probably should include:

1) Addition of the degradation reaction of the liquid tar inside the particle and the deactivation of the activated coal. This was proposed above in the general scheme, but then had to be set aside because of the lack of experimental data against which to test the theory.

2) Characterization of the physical processes like tar vaporization, heat transfer to and inside the coal, and the diffusion of the volatile matter out of the coal particle. This would allow the investigation of the influences of bed height, pressure and particle size on yields and a determination of those conditions in which physical processes are rate controlling.

3) Identification of the general compounds (tar,gas, solid) in terms of chemical species in order to distinguish between more or less desirable pyrolysis products. This more detailed formulation of the reactions can also lead to the determination of the heats of reaction.

It will not be possible to accomplish these points by using only experimental data presently available in the open literature. To refine and extend our kinetic model, new experiments will have to be designed and conducted. However,our kinetic scheme helps to identify the important parameters that will have to be properly considered in new experiments. These parameters will include the identification of the volatile matter with respect to tars, gases and liquors, possibly even with respect to specific chemical species, and the effects of the particle size and the pressure.

The importance of a good chemical-kinetic (and thermochemical) scheme is that it can be applied to the theoretical modeling of coal conversion processes. This will include the coupling of the chemical kinetic model with models of flow reactors, such as fluidized beds, fixed beds (co-current or counter-current), and entrained flow reactors. Because of the distinction between tars and different gases, our model is readily applicable for the optimization of coal liquefaction and coal gasification processes. With a further refinement of the model the possible goals for optimization can be extended, e.g. an optimization towards a maximum economic value of all the pyrolysis products would be possible. The reactor designer can use this kind of model also for controll calculations, i.e., how to achieve optimum yield or how to avoid undesired reactor instabilities (using the equations in dynamic form). Our approach to the modeling of the gas phase degradation is a first example (as described above) of the coupling of the chemical kinetic scheme with a simplified flow reactor model.

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NOMENCLATURE

A	=	Frequency factor, sec^{-1}
AC	=	Mass fraction of activated coal, $g_{AC}/g_{Start.Material}$
$B_{1,2}$	=	Empirical constants used by Badzioch
B_3	=	Residual volatile matter in the char
C	=	Mass fraction of coal, $g_C/g_{Start.Material}$
C_0	=	Initial mass fraction of coal, $g_C/g_{Start.Material}$ (normally = 1)
E	=	Activation energy, kcal/mole
f_i	=	Rate at which compound i is produced or consumed, g_i/sec
m	=	Heating rate, K/sec
M_i	=	Molecular weight of gaseous species i, g/mole
k_j	=	Rate constant of reaction j, sec^{-1}
P	=	Pressure, g/cm^2
PG	=	Mass fraction of primary gas, $g_{PG}/g_{Start.Material}$
PR_i	=	Production rate of gaseous species i due to primary decomposition, $g_i/cm^3_{Reactor}$-sec
PT	=	Mass fraction of primary tar, $g_{PT}/g_{Start.Material}$
R	=	Gas constant, kcal/moleK
RP_i	=	Reaction rate of species i in the gas phase, $g_i/cm^3_{GasPhase}$-sec
S_i	=	Mass fraction of solid intermediate i or solid residue i, $g_S/g_{Start.Material}$
t	=	Time, sec
T	=	Temperature, K
T_M	=	Temperature of maximum gas release rate, K
u	=	Flow velocity in the gas phase, cm/sec
V	=	Gas volume released by a thermal degradation reaction (varying with time), cm^3/g_{Mat}

V_0 = Maximum possible gas volume from a thermal degradation reaction, cm^3/g_{Mat}

VM = Mass fraction of volatile matter, $g_{VM}/g_{Start.Material}$

VM_0 = Proximate volatile matter (ASTM standard), %

W = Weight loss

x = Stoichiometric coefficient (by mass for reactions 1-5) (molar for reactions 6-7)

y_i = Stoichiometric coefficient for the solid residue produced by the gas phase degradation.

Y_i = Mass fraction of gaseous species i in the gas phase

ρ = Density in the gas phase

ν = Void space in the gas phase

Table I

Kinetic parameters for the pyrolysis model of Kobayashi (Ref. 25)

KINETIC PARAMETER	REACTION I	REACTION II
Activation Energy E (kcal/mole)	17.6	60.0
Frequency Factor A (sec^{-1})	2.2×10^5	2.0×10^{12}
Stoichiometric Coefficient x	0.39	1.0
Heat of Reaction ΔH (cal/g coal)	-412.	-200.

TABLE II

GENERAL HYPOTHETICAL SCHEME FOR COAL PYROLYSIS

C	$\xrightarrow{k_1}$	AC	Activation Step (high E)
AC	$\xrightarrow{k_2}$	$x_2PT_L + (1 - x_2)S_1$	primary decomposition — low E
AC	$\xrightarrow{k_3}$	$x_3PG_2 + (1 - x_3)S_2$	primary decomposition — medium E
S_1	$\xrightarrow{k_4}$	$x_4PG_2 + (1 - x_4)S_3$	primary decomposition — high E
S_2	$\xrightarrow{k_5}$	$x_5PG_3 + (1 - x_5)S_4$	primary decomposition — high E
AC	$\xrightarrow{k_6}$	DAC	Deactivation Step (DAC $\neq$ C)
PT_L	$\xrightarrow{k_7}$	$x_7SG_1 + Y_7S_5$	Polymerization in the liquid phase inside the particle
PT_L	$\xrightarrow{k_8}$	PT_G	Vaporization (depending on heat and mass diffusion)
PT_G	$\xrightarrow{k_9}$	$x_9SG_2 + Y_9S6$	Polymerization in the gas phase
PT_G	$\xrightarrow{k_{10}}$	$x_{10}SG_3 + Y_{10}S_7$	Cracking in the gas phase

where

C = Initial coal
AC = Activated coal
PT_L = Liquid primary tar
PT_G = Gaseous primary tar
PG = Primary gas
SG = Secondary gas
S = Solid intermediate or residue
x,y = Stoichiometric coefficients
AE = Activation energy

TABLE III

SIMPLIFIED SCHEME FOR COAL PYROLYSIS

$$
\left.\begin{array}{lll}
C & \xrightarrow{K_1} & AC \\
AC & \xrightarrow{K_2} & x_2\ PT + (1 - x_2)S_1 \\
AC & \xrightarrow{K_3} & x_3\ PG_1 + (1 - x_3)S_2 \\
S_1 & \xrightarrow{K_4} & x_4\ PG_2 + (1 - x_4)S_3 \\
S_2 & \xrightarrow{K_5} & x_5\ PG_3 + (1 - x_5)S_4
\end{array}\right\} \text{PRIMARY DECOMPOSITION}
$$

$$
\left.\begin{array}{lll}
PT & \xrightarrow{K_6} & x_6\ SG_1 + Y_6\ S_5 \\
PT & \xrightarrow{K_7} & x_7\ SG_2 + Y_7\ S_6
\end{array}\right\} \text{SECONDARY DECOMPOSITION IN THE GAS PHASE}
$$

TABLE IV

SELECTION OF KINETIC VALUES FOR REACTION

E_1 (kcal/mole)	A_1 (sec^{-1})	m (C/sec)	T (K)	$\frac{C}{C_0} = \frac{V_0 - V}{V_0}$
70.	$3 \cdot 10^{18}$	$4.2 \cdot 10^{-5}$	633.	0.538
		$4.3 \cdot 10^{-4}$	673.	0.199
		$1.5 \cdot 10^{-2}$	703.	0.624
		35000.	973.	0.653
		45000.	1173.	0.0
75.	$2 \cdot 10^{20}$	$4.2 \cdot 10^{-5}$	633.	0.537
		$4.3 \cdot 10^{-4}$	673.	0.0925
		$1.5 \cdot 10^{-2}$	703.	0.442
		35000	973.	0.136
		45000	1173.	0.0
80.	$2.4 \cdot 10^{21}$	$4.2 \cdot 10^{-5}$	633.	0.877
		$4.3 \cdot 10^{-4}$	673.	0.530
		$1.5 \cdot 10^{-2}$	703.	0.774
		35000.	973.	0.185
		45000	1173.	0.0

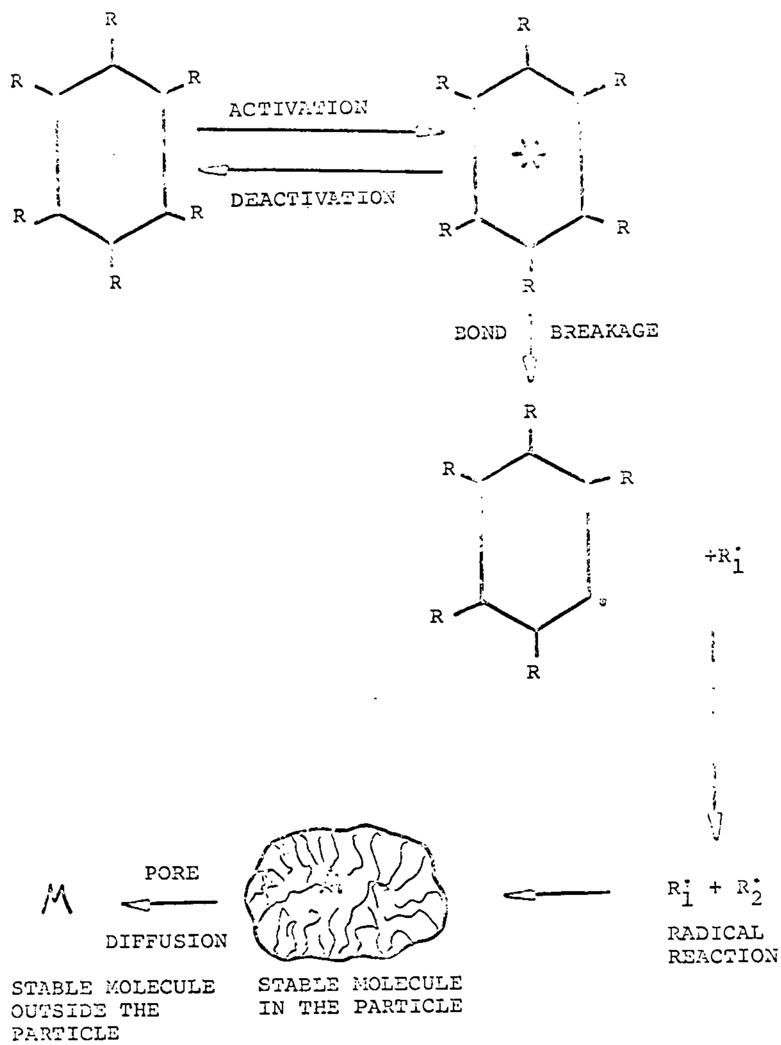

FIG. 1 MECHANISM OF COAL PYROLYSIS (JUENTGEN, VAN HEEK, [22])

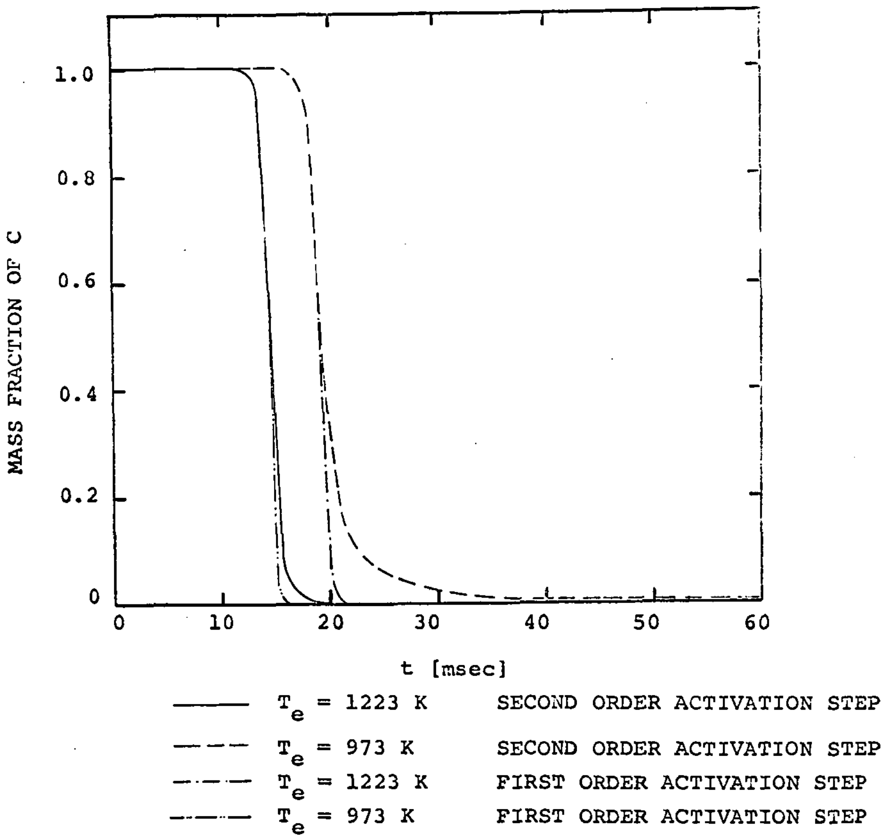

FIG. 2 INFLUENCE OF THE REACTION ORDER OF THE ACTIVATION STEP ON THE CONVERSION OF COAL TO ACTIVATED COAL.

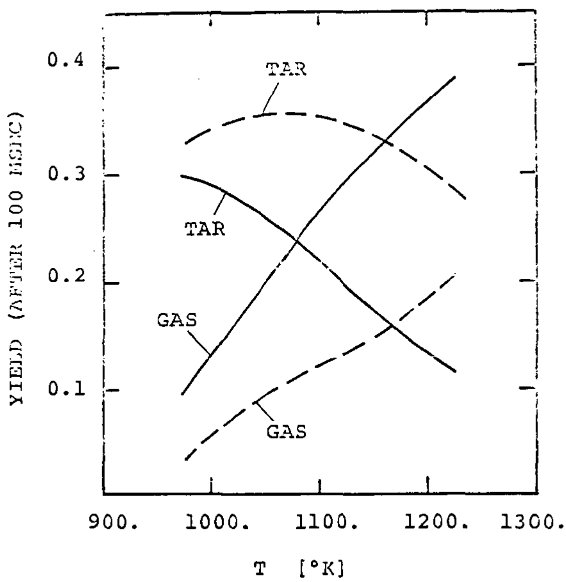

FIG. 3 VARIATION OF THE KINETIC VALUES OF REACTIONS 2 AND 3.

———————— E_2 = 5. kcal/mole E_3 = 30. kcal/mole

– – – – – – E_2 = 10.7 kcal/mole E_3 = 40. kcal/mole

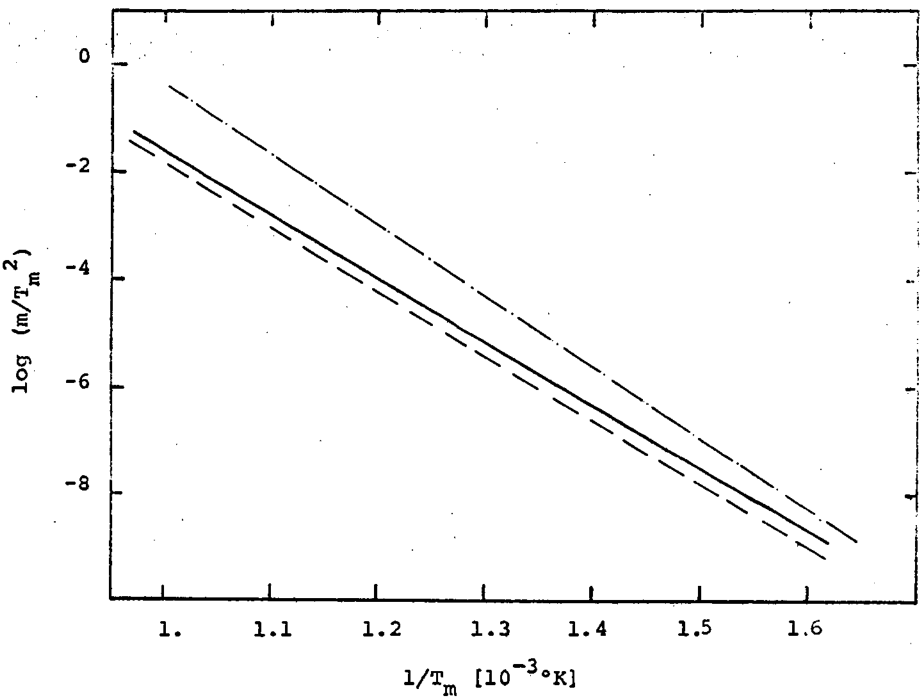

FIG. 4 INFLUENCE OF THE HEATING RATE m ON THE TEMPERATURE OF MAXIMUM GAS RELEASE T_m.

——— THEORETICAL RESULTS

– – – – EXPERIMENTAL RESULTS FOR CH_4 FORMATION [2]

–·–·–·– EXPERIMENTAL RESULTS FOR C_2H_6 FORMATION [2]

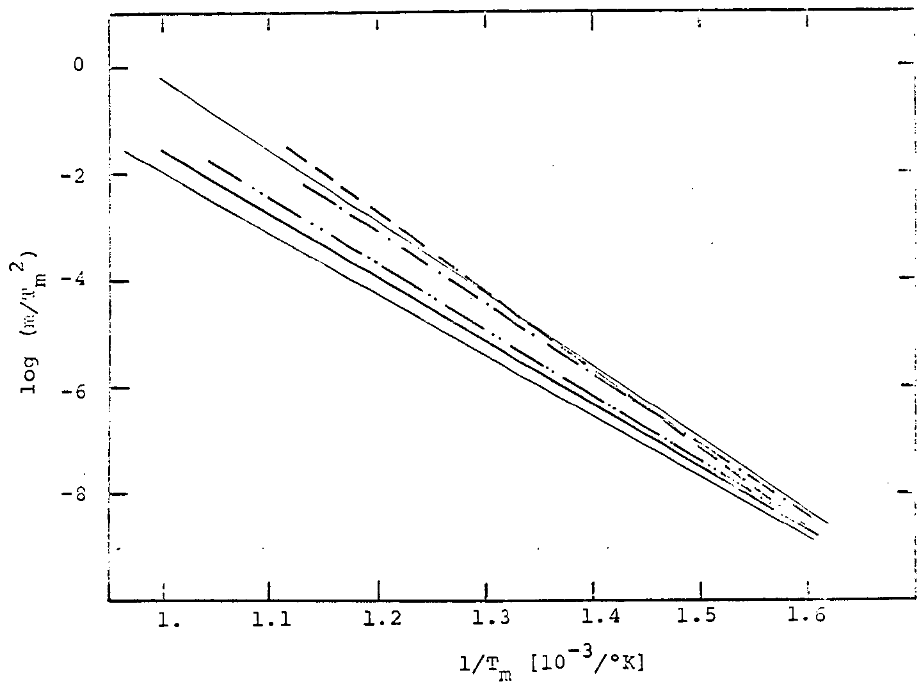

FIG. 5 INFLUENCE OF E_4 ON THE RELATION BETWEEN T_m AND m.

— — — — E_4 = 37. kcal/mole
-·—·—·— E_4 = 43.7 kcal/mole
-··—··— E_4 = 50. kcal/mole
———— E_4 = 55. kcal/mole
———— Experimental results for CH_4 and C_2H_6 [2]

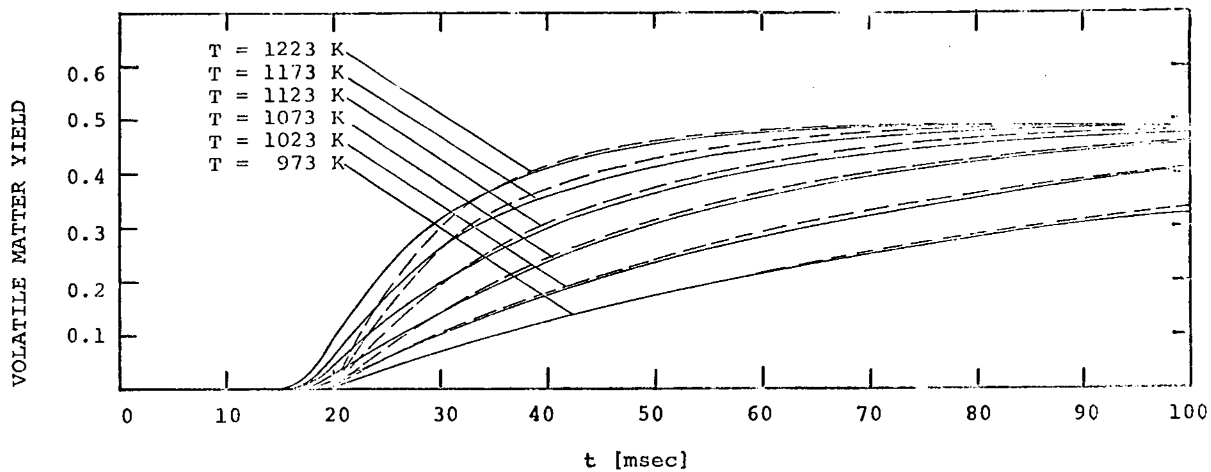

FIG. 6 PRIMARY DECOMPOSITION OF A hvAb COAL AT DIFFERENT TEMPERATURES

——— THEORECTICAL CURVE CALCULATED WITH PRIMARY DECOMPOSITION SCHEME

— — — EXPERIMENTAL CURVE OBTAINED BY BADZIOCH AND HAWKSLEY [11] FOR COAL D

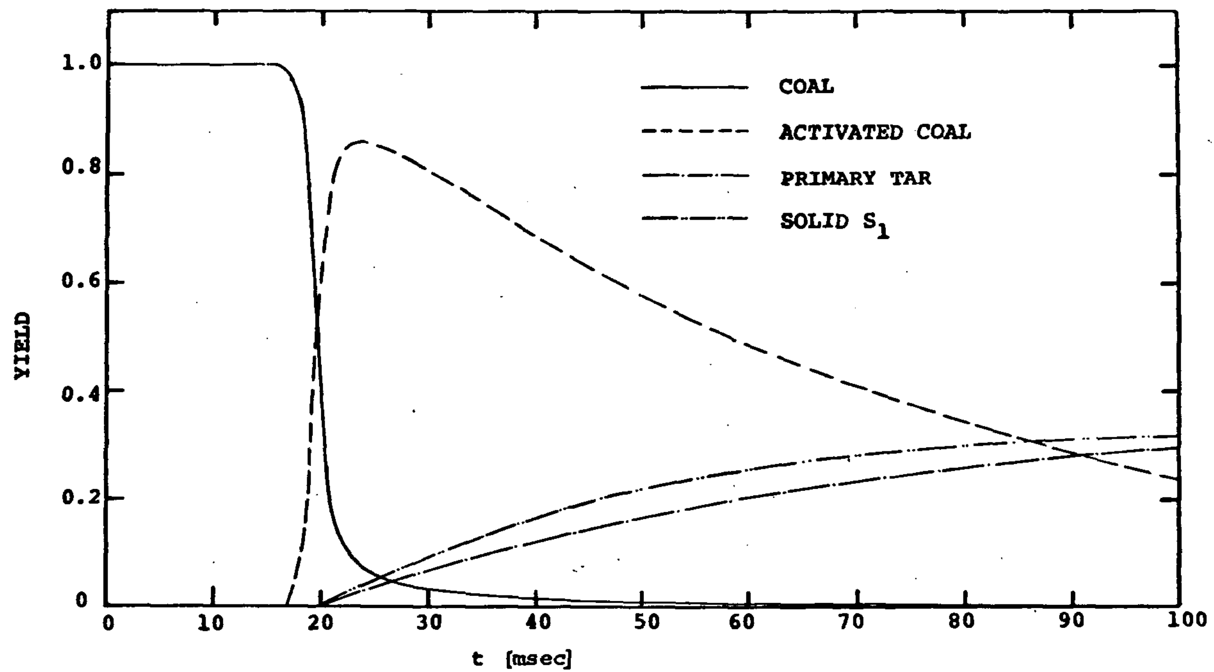

FIG. 7 PRIMARY DECOMPOSITION AT T = 973°K PRODUCT DISTRIBUTION

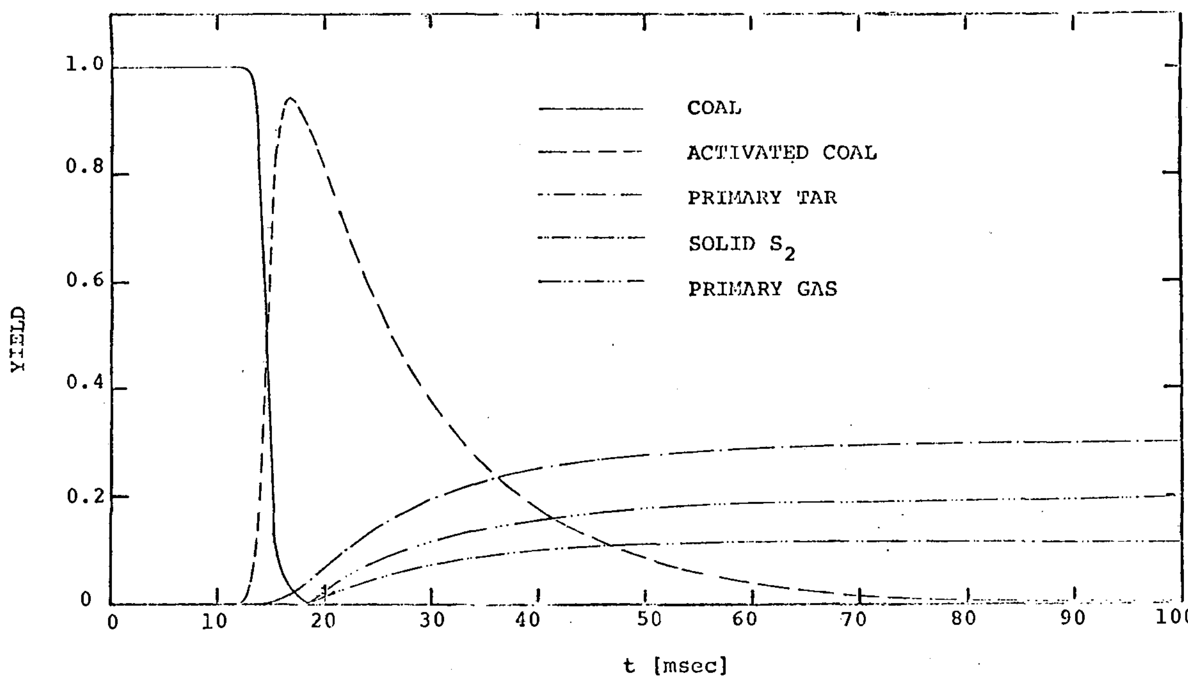

FIG. 8 PRIMARY DECOMPOSITION AT T = 1223°K PRODUCT DISTRIBUTION

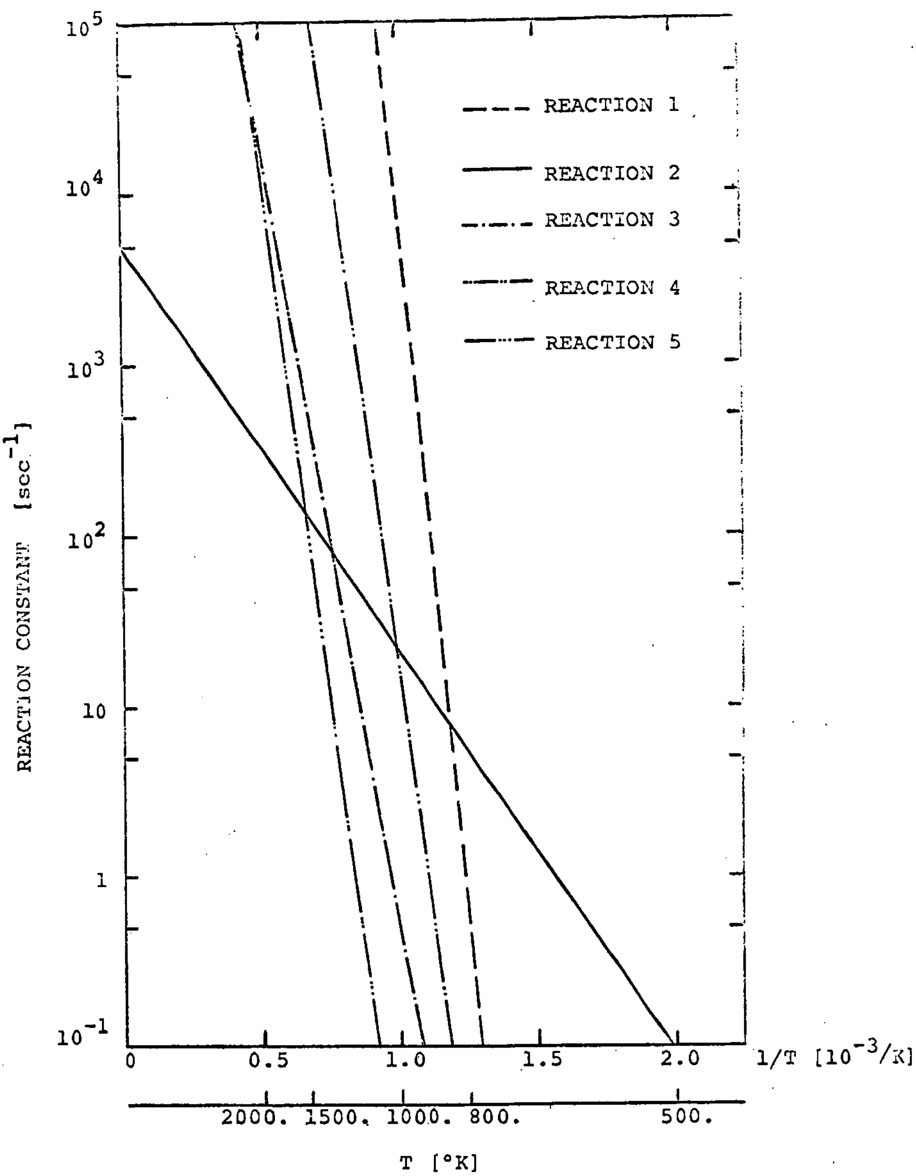

FIG. 9 REACTION CONSTANTS FOR THE PRIMARY DECOMPOSITION REACTIONS 1-5.

PRELIMINARY SMALL-SCALE COMBUSTION TESTS OF COAL LIQUIDS

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1.0 INTRODUCTION

Because of recent intense concern for environmental conservation, air pollutants which originate from combustion sources have attracted a great deal of attention, including sulfur oxides, nitrogen oxides (NO_x), and smoke particulates. Emission factors for stationary sources have been determined which relate the rate of pollutant emission to the types of boilers and furnaces and grades of fuel oils and other fuels.[1] Studies have demonstrated that NO_x emissions arise from two sources: (1) molecular nitrogen in the combustion air is oxidized via a thermal process to form "thermal NO_x"; and (2) nitrogen which is chemically bound in the fuel is converted to "fuel NO_x".[2,3,4] The most effective approach to eliminating NO_x emissions from combustion sources is the modification of the combustion process. Several combustion modification techniques have been developed to combat NO_x emissions, and staged combustion has been shown to be the most effective technique for the suppression of the oxidation of fuel nitrogen.[5,6] The smoking tendencies of fuel oils have been related to their API gravity and other properties.[1,7]

The growing imbalance between energy consumption and fuel production has created a need to supplement petroleum-derived fuels by the conversion of coal and other fossil fuel forms into liquid fuels. Studies by many organizations, including the Gulf Oil Corporation, have shown that low severity processing is sufficient to convert coal to a low sulfur liquid fuel. However, such liquids still differ from conventional petroleum-derived fuel oils in the same viscosity range; the coal liquids contain more nitrogen and aromatic compounds, being hydrogen deficient. As a result, the combustion of such liquids can be expected to produce greater emissions of NO_x and smoke and will require upgrading to produce suitable fuel products.

In order to obtain more information about the relationships between coal liquid composition and combustion emissions, we have submitted several coal liquids to the combustion tests to be described in this paper. In these tests a modified one-gph (3.8 dm^3h) residential boiler was used, which required relatively small samples; the coal liquids were tested as produced and were in the quality range of a No. 4 fuel oil. Thus, these tests are preliminary in nature, and neither the boiler nor the liquids used are intended to represent future commercial equipment or fuel products. The results of these tests of coal liquids are instead to be interpreted by referring to some tests of conventional petroleum-derived fuel oils in the same boiler, which served to "calibrate" it. Some operating parameters of the burners and boiler were also varied to further establish their role in the combustion behavior of the coal liquids.

2. EXPERIMENTAL

2.1 EQUIPMENT AND PROCEDURES

The structure of the test boiler and associated equipment used is shown in Figure 1. The burner was fired horizontally into a firebrick-lined combustion chamber 38cm (15 in.) long, 28cm (11 in.) wide, and 35.5cm (14 in.) high; the flame gases then passed upward into the boiler section, where they were cooled to 230-290°C (450-550°F). Gases were sampled from the flue immediately above the boiler section, and were delivered through 6.25mm O.D. stainless steel tubing to an ice bath and a train of continuous analyzers for NO_x (electrochemical or chemiluminescent), CO_2 and CO (NDIR), and O_2. Instrument accuracy was verified with Orsat readings for CO_2 and CO, and by comparison with combustion stoichiometric calculations. A Bacharach smoke number sampler (ASTM D 2156) was also positioned in the flue; smoke filter discs were read photometrically. The low velocity of the flue gases made isokinetic sampling impractical.

A modified residential "gun-type" burner was used, which had a motor-driven fan. The small orifice of the pressure-atomizing nozzle tended to become plugged by the coal liquids; and it was necessary to substitute an air-atomizing nozzle, which had no small orifices. This burner was also equipped with an efficient flame retention head, which was so positioned that all the combustion air emerged through it into the combustion chamber. Although this produced a high swirl and turbulence in the flame, it permitted measurements at low excess air levels without the formation of excessive smoke, which would tend to degrade the reliability of the flue gas analysis instruments. (The behavior of other burners with less air turbulence was also ascertained; these are described in Section 3.2) A further advantage of the air-atomizing nozzle (compared to pressure-atomizing nozzles) is the independent variability of fuel flow (which was controlled by a peristaltic pump), atomizing pressure, and fuel viscosity.

In a typical run, the fuel flowrate was held constant at 3.8 dm^3/h (1.0 gph), and the combustion air input was varied. The atomizing air pressure was 34.4kPa (5 psi) unless otherwise noted. The boiler was fired initially with No. 2 fuel oil to bring the system to equilibrium before introducing samples. Periodically, the No. 2 oil was fed into the system to check instrumentation and to serve as a reference. During a run, the combustion air was varied and measurements of Smoke Number, CO, CO_2, O_2, NO_x, and unburned hydrocarbon were taken. At each change of the air gate opening or other operating variable, the excess air level was calculated in the conventional manner from the measured CO_2 and the C/H content of the test fuel.

In addition to the measured total concentrations of NO_x in the flue gas, a parameter of interest is the portion of the NO_x which originated from the fuel nitrogen and the fraction of the fuel nitrogen which was converted to NO_x (the remainder of the fuel nitrogen emerging as N_2). The concentration of thermal-NO_x in the flue gases from the combustion of the test fuel was assumed to be the same as that measured in the combustion of No. 2 fuel oil, and was subtracted from the total value to obtain the fuel-NO_x concentration. (Two slight differences between the combustion of No. 2 fuel oil and of coal liquids which are neglected in this procedure are the different volumes of dry stack gases and the different flame temperatures, resulting from the use of the same volumetric fuel feed rate but different heat input rates. The resulting error is estimated to be less than 5%.) The fraction of fuel nitrogen converted to NO_x was obtained as the ratio of the observed fuel-NO_x concentration and the theoretical fuel-NO_x concentration computed for complete conversion by combustion stoichiometry. The nitrogen contents of the test fuels were determined by Kjeldahl analyses.

2.2 PROPERTIES OF FUELS

The properties of the fuels tested are listed in Table I. The coal liquids were produced in a bench-scale version of the Gulf Catalytic Coal Liquefaction process, which is based on the hydrogenation of a pulverized coal-solvent slurry. These liquids contained less than 0.1% sulfur. Samples F1 and F2 are filtered full boiling range process effluents; they were produced from western subbituminous and Pittsburgh Seam bituminous coals, respectively. These full-range liquids contained 0.5% nitrogen, and their viscosities were in the range of No. 4 or No. 5 fuel oils. Coal liquid "D" was a 130-350°C (270-670°F) distillate obtained from the full-range liquid F1; it contained 0.31% nitrogen and its viscosity was near that of No. 2 fuel oil.

3. RESULTS AND DISCUSSION

3.1 EMISSIONS FROM COAL LIQUIDS

Emissions of sulfur dioxide were very low because of the low sulfur content of these liquids. The concentrations of carbon monoxide and hydrocarbons in the flue gases were less than 5 ppm except at times when the smoke number exceeded eight. The smoke data are presented in Section 3.1.3; these coal liquids produced much less smoke than that which is encountered while burning typical petroleum-derived fuel oils having such low API gravities (7-14°API). When the excess air was greater than 25%, a relatively low air requirement, the smoke from the distillate and full-range coal liquids was within the limits corresponding (respectively) to home furnaces and industrial uses. The only emission which seemed to be problematic was NO_x.

3.1.1 Conversion of Fuel-Bound Nitrogen

The NO_x concentrations in the flue gas measured in the tests of the coal liquids in the air-atomizing test burner are shown in Figure 2. The distillate produced between 250 and 300 ppm of NO_x, and the full-range liquids produced between 300 and 400 ppm of NO_x. The emissions from No. 2 fuel oil are also shown. The concentration of NO_x in the flue gas did not vary greatly with excess air, but correction for dilution by excess air shows (Figure 3) that the amount of NO_x emitted from the burning of coal liquids increased with excess air; this was due to increased oxidation of the fuel-bound nitrogen. The amount of thermal NO_x produced by the No. 2 fuel oil decreased with increasing excess air, due to cooling of the flame by the additional air.

The effects of the nitrogen content of the fuels and of the excess air levels in the tests can best be seen in Figure 4, which presents the fraction of fuel nitrogen converted to NO_x as a function of the excess air level. We first compare the behavior of the coal liquids and petroleum fuels when the excess air was 25%. Thirty-two and forty percent of the nitrogen in the full-range coal liquids was converted to NO_x. These conversion values are close to those for 0.5% nitrogen petroleum oils reported by Turner and Siegmund;[3] in that study, a 10-gph boiler was used, which contained an insulation-lined combustion chamber and an air-atomizing nozzle. The fuel nitrogen conversion exhibited by the distillate coal liquid in our tests was 52%, which is higher than that of the full-range liquids; this value is also close to that of a petroleum fuel oil containing 0.3% nitrogen, observed by Turner and Siegmund.[3] These values for fuel nitrogen conversion in the coal liquids are also consistent with the observation by others that more of the fuel nitrogen is converted in less nitrogen-rich fuels.[2,3,6] It is possible that the test unit used in this study and in the large unit reported in Reference 3 involves flames which are similar in aspects that affect fuel nitrogen conversion; if so, one can conclude that the NO_x emissions from coal liquids will generally resemble that from petroluem fuel oils in such boilers. Observations of the effects of burner operating parameters are described in Section 3.2.

Thus, the distillate coal liquid contained only 60% as much nitrogen as the full-range coal liquids, but it yielded nearly as much NO_x in combustion, as a result of the higher fuel nitrogen conversion associated with its lower nitrogen concentration.

In addition to the effect of the nitrogen concentration on the conversion levels, other differences between the distillate and full-range liquids may have influenced the nitrogen conversions in these liquids. The viscosity of the full-range liquid was four times that of the distillate, and from a correlation for pneumatic atomizers,[8] it was estimated that the mass mean diameter of the droplets in the filtrate spray was twice that of the distillate droplets. Furthermore, the droplets of the full-range liquid probably volatilized in the flame more slowly than those of the distillate.

There are also a few indications of effects of the volatility and composition of the nitrogen compounds in the fuels. Approximately one-half of the nitrogen compounds in the full-range liquid F1 boiled above 350°C (670°F), in contrast to the nitrogeneous components of the distillate, which of course all boiled below that temperature. Tests of pyridine-doped No. 2 fuel oil in the test burner (curve "10" in Figure 7) also indicate that the pyridine was more extensively oxidized than were the nitrogen compounds in the distillate coal liquid. [The conversion of the 0.5% N oil (as pyridine) was close to the nitrogen conversion level (52% at 25% excess air) of the distillate coal liquid (which contained 0.3% nitrogen), and the conversion of 0.3% N oil (as pyridine) would then definitely exceed 52%.] Finally, in three of the burners employed in tests described in Section 3.2, the conversion of piperidine in No. 2 fuel oil was 10-15% greater than the conversion of pyridine; the dopant level was 0.50% N in both cases, and this difference occurred only between 50% and 100% excess air.

3.1.2 Effect of Excess Air

The major operating parameter which affects combustion emissions is the excess air level. In tests of the coal liquids in the test burner, between 70% and 80% of the fuel nitrogen in all the coal liquids was converted to NO_x at very high excess air levels. The fuel nitrogen conversion exhibited by the distillate liquid decreased regularly to 40% as the excess air level was reduced to 6%. These conversion levels are close to those observed by Turner and Siegmund.[3] They also found that the conversion continued to decrease as the air feed was reduced below stoichiometric values, in a simulation of the first stage of staged combustion; this accounted for the success of this technique. The conversion of the fuel nitrogen in the full-range coal liquids exhibited a similar response to decreasing excess air, although in the lower excess air range, its decrease appears to be unusually rapid. Others have also noted dramatic decreases in conversion with decreasing excess air.[5] Thus, staged combustion may serve to limit the NO_x emissions arising from the nitrogen in coal liquids. This technique is also likely to be more effective in larger furnaces whose residence time is longer than that of the test unit used here. However, staged combustion is limited by the soot formed in the fuel-rich first stage, and this limitation will become problematic with coal liquids.

3.1.3 Smoke Emissions

The smoke measurements made during these tests of the coal liquids in the test burner are shown in Figure 5. Data are also included from tests of anthracene oil and No. 4 fuel oil [the latter at 138kPa (20 psi) atomizing air pressure]. No. 2 fuel oil gave no smoke when the excess air exceeded 12%. When the excess air was greater than 25%, the smoke from the distillate coal liquid was less than ASTM smoke No. 1 (a typical performance requirement for a home furnace) and the smoke from the full-range liquids was less than approximately a Ringelman number one, which is a common limit for industrial furnaces. This is a relatively low air requirement. When the excess air was increased above 50%, the smoke from the distillate fuels (including anthracene oil) decreased to less than ASTM smoke No. 1; in contrast, the residual fuels (the full-range coal liquids and the No. 4 fuel oil) produced moderately persistent smoke.

There is a relationship between the smoking tendencies of these fuels and some of their compositional properties. The most influential of these properties is apparently the non-volatile content of the full-range fuels, whose persistent smoking places them in a separate group from the distillate fuels. Further comparisons of smoke formation from full-range coal liquids and from petroleum residual fuels are needed and may be made possible by using a variable fuel preheater in the test burner. The API gravity of the distillate fuels is closely related to their tendency to form soot in the low excess air range. Viscosities and carbon numbers do not seem to bear any regular relation to the smoking tendencies of this set of fuels, although these properties are also important.

In order to obtain further information about the effect of the aromatic content of fuels on their smoking tendencies, a middle distillate cycle oil was tested. It resembled the distillate coal liquid, since its API gravity was 15.3; but it did not plug pressure-atomizing nozzles, permitting the use of a conventional but efficient home furnace burner. No. 2 fuel oil was also burned for comparison. The No. 2 fuel oil required 17% excess air to limit the smoke from its combustion to a number one spot; and the cycle oil required a moderate increase in excess air, to 27%, to reduce its smoke to this limit.

3.2 EFFECT OF BURNER DESIGN ON EMISSIONS

As we have described, the combustion of the coal liquids in the residential-size test burner produced fuel nitrogen conversion levels which were close to the conversions reported for residual petroleum fuel oils burned in somewhat larger units. These latter furnaces had air-atomizing nozzles; and in comparison with residential burners, they had longer residence times and higher flame temperatures. In contrast, tests by Martin[2] in a representative residential furnace produced fuel nitrogen conversions which were generally 50% lower then those observed in our modified residential test furnace and in the larger units mentioned above. A pressure-atomizing nozzle was employed by Martin to burn a series of No. 2 fuel oils doped with pyridine and other nitrogen compounds; this unit had a high tendency to form smoke.

On the other hand, much greater fuel nitrogen conversion has been observed in small combustors in which very high combustion intensities were produced by accelerated mixing of combustion air and fuel, and also by the fine atomization of the oil.[4,9] In such units between 50% and 100% of the fuel nitrogen was converted to NO_x. In order to relate our results to these various studies, several burners were assembled having various air handling parts which varied the air mixing rate over a wide range; these burners were used in a series of tests with No. 2 fuel oil doped with pyridine at the level of 0.50% nitrogen. Since the smoke-forming tendency of such burners decreases with an increasing air fuel mixing rate, the smoke number curve of each burner was used to empirically characterize its mixing rate as shown in Figure 6. Each burner is designated by the excess air level which it required to reduce the smoke to a number one spot; for example, the test burner used in the coal liquids test required only 10% excess air, while the least efficient residential burner required 120% excess air. Pressure-atomizing nozzles were employed in all burners except Unit "10", and the droplets produced by the former were probably several times larger than those produced by the air-atomizing nozzle in Unit 10. Burners 40A, 40B, and 120 were fired in the same test boiler as Unit 10, but had various air handling parts and/or flame retention heads. Curve "75" is plotted from data obtained[10] from the test furnace employed by Martin and Berkau in the tests of pyridine-doped No. 2 fuel oil which we cited above.[2]

Each of these burners was used to fire No. 2 fuel oil which contained 0.5% nitrogen as pyridine; Figure 7 displays the fuel nitrogen conversion observed in each burner plotted as a function of excess air. At any excess air value, the fuel nitrogen conversion was greater in burners having lower smoking tendencies or faster air-fuel mixing. For example, at 50% excess air, Burner 120, which produced the most smoke, converted only 35% of the fuel nitrogen to NO_x. In contrast, in Unit 10, the fuel nitrogen conversion to NO_x was 70%.

4.0 CONCLUSIONS

In the following, we summarize the observations made with the particular fuels and boiler used here, and note some implications of these results.

1. Generally, the combustion of the coal liquids produced negligible amounts of sulfur oxides (because of their low sulfur content) and CO and hydrocarbons. The amount of smoke from the combustion of the distillate and the full-range liquids was less than the typical limits for (respectively) home furnaces and for industrial units. Only the NO_x emissions were potentially problematic. This problem can be solved with the removal of nitrogen from some coal liquids by upgrading; the minimum processing requirements for this are now being ascertained.

2. The coal liquids tested contained 0.3% and 0.5% nitrogen, and the concentration of NO_x in the flue gas resulting from their combustion ranged between 240 and 400 ppm. The behavior of the coal liquids in the test burner used here was similar to that observed by Turner and Siegmund in their tests of petroleum residual oils in a 10-gph boiler. At 25% excess air, 35% to 50% of the fuel-bound nitrogen was converted to NO_x. Although the nitrogen content of the distillate coal liquid was 40% less than that of the full-range liquid, NO_x emissions from the former were not appreciably reduced. The reduction in NO_x emissions with decreasing excess air suggests that staged combustion will be effective when applied to coal liquids combustion, although smoke formation may then be problematic.

3. Pyridine-doped No. 2 fuel oil exhibited more extensive conversion to NO_x than did the distillate coal liquid, probably due to the lower volatility of the nitrogen content of the latter. Piperidine appeared to exhibit slightly higher conversion than did pyridine, at high excess air levels. There was little difference between the emissions from the combustion of full-range liquids derived from bituminous and sub-bituminous coal.

4. Tests of pyridine-doped No. 2 fuel oil in a series of modified burners showed that as the fuel-air mixing rate was increased and smoke formation decreased, the conversion of fuel nitrogen was doubled. The fuel-air mixing rate in the test burner used in the coal liquids tests was greater than that in conventional home furnace burners.

In conclusion, these tests of coal liquids illustrate how several fuel properties and equipment and operating parameters affect the emissions of NO_x and smoke from these fuels. These effects are similar to those noted in others' observations of the combustion of petroleum fuel oils, although more definitive testing is indicated.

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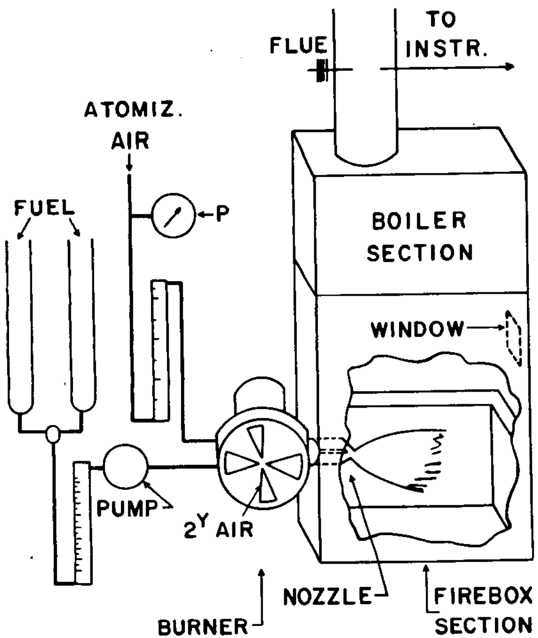


FIGURE I
RESIDENTIAL BOILER AND ASSOCIATED EQUIPMENT

FIGURE 2
MEASURED NO_x CONC.

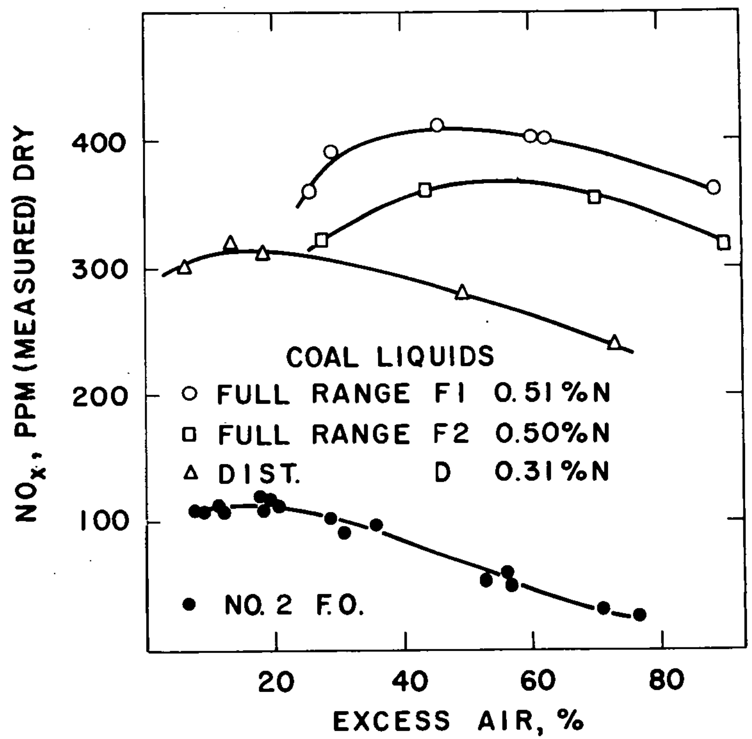


FIGURE 3
AMOUNT OF NO_x

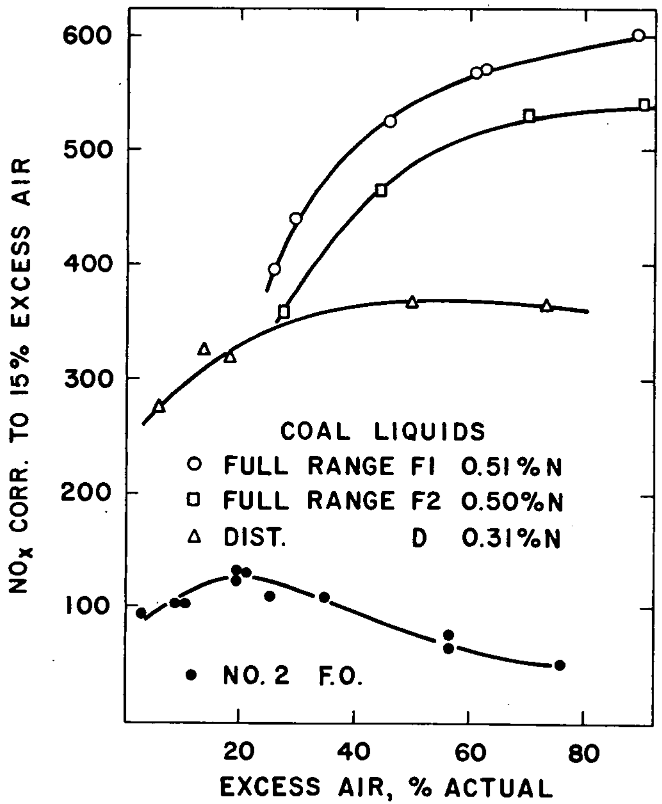


FIGURE 4
CONVERSION OF FUEL-N

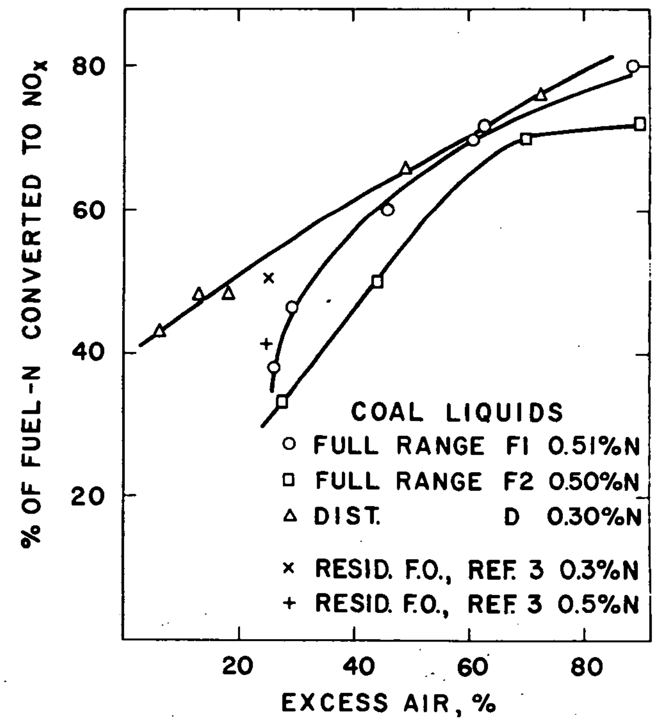


FIGURE 5
SMOKE FROM COAL LIQUIDS AND OTHER FUELS

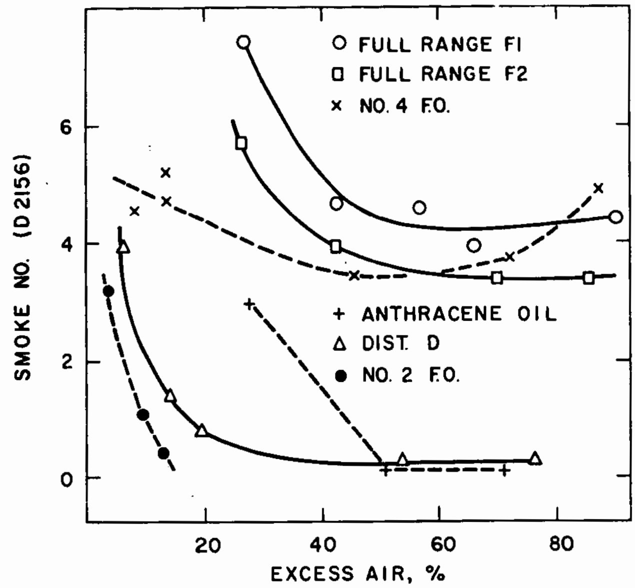
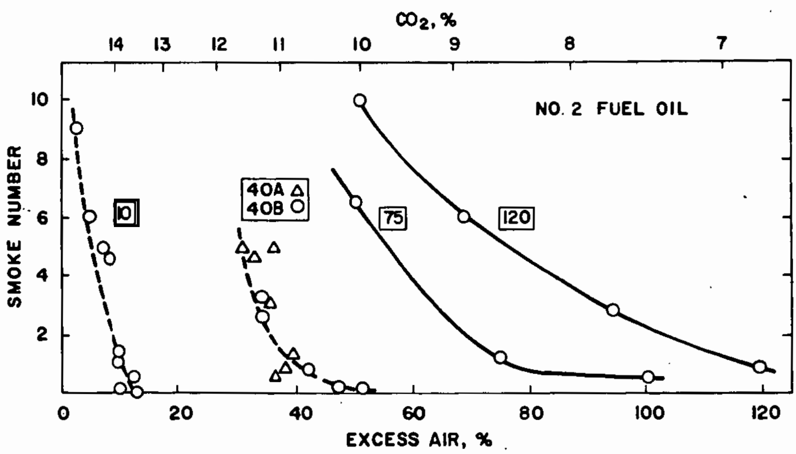


FIGURE 6
SMOKE FROM VARIETY OF BURNERS



BURNER 10: AIR ATOMIZING NOZZLE - 1 GPH
OTHER BURNERS: PRESSURE ATOMIZING NOZZLES - 1 GPH
BURNER 75: WASSER, ET. AL., REF. 10, 0.75 GPH

FIGURE 7
EFFECT OF BURNERS ON FUEL-N CONVERSION

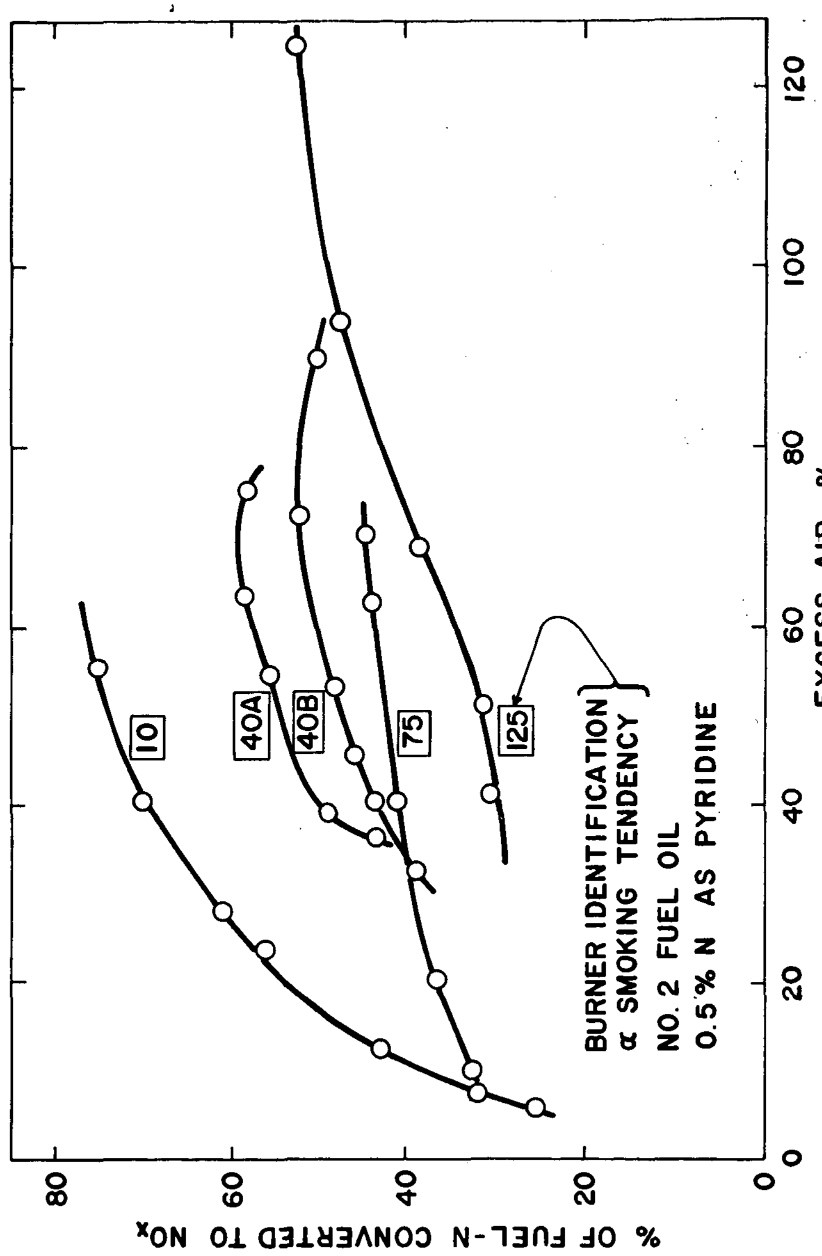


Table I

PROPERTIES OF FUELS TESTED

	Coal Liquids						
	Distillate D	Full-Range F1	F2	Anthracene Oil	Cycle Oil	No. 2 Fuel Oil	No. 4 Fuel Oil
Gravity °API	14.1	7.0	10.4	-	15.3	34.5	28.3
Density, 15°C (kg/l)	0.9730	1.0217	0.9970	-	0.9638	0.8524	0.8854
Ash %w	.0030	0.010	.013	.002	-	-	-
Carbon %w	89.56	89.93	89.0	91.02	90.7	86.9	86.41
Hydrogen %w	9.54	8.84	9.44	5.90	9.3	13.1	12.36
Nitrogen %w	0.31	0.51	0.50	0.98	-	0.01	-
Sulfur %w	.04	0.07	-	0.58	0.50	0.10	-
Dist. Range, °C	130-364	-	-	>200	204-338	182-338	-
(°F)	(266-688)	-	-	(>392)	(400-640)	(360-640)	-

COMPARISON OF EVOLUTION OF HETEROATOMS FROM COAL AND PETROLEUM-BASED ELECTRODE COKES. G. M. Kimber, M. D. Gray, National Coal Board, Coal Research Establishment, Stoke Orchard, Cheltenham, Glos. England.

A route for making, from coal, a high-purity coke suitable for the manufacture of both graphite and carbon electrodes has been developed by the National Coal Board at its Coal Research Establishment in England. This process for electrode coke involves the solvent extraction of coal and is part of a wider NCB programme into the beneficiation of coal which includes, besides electrode coke, hydrocarbon products, chemicals and carbon fibres. This paper describes the heat treatment of cokes in the range 1300 - 2500°C and shows that the heteroatoms in coal-based electrode cokes are bound to the carbon structure in a different manner to those in petroleum coke. By measuring the growth of graphitic crystallites by x-ray diffraction, it is also shown that the rate of graphitisation is similar for both types of coke.

KINETICS OF COAL LIQUEFACTION

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INTRODUCTION

Information on the rates of coal dissolution which is needed in the design of reactors in a coal liquefaction plant has been very limited; therefore, methods are needed by which dissolution rate data can be extrapolated to other operation conditions. In this section, the rates of solvation of coal in various oils under hydrogen pressure without the presence of catalyst are examined.

The role of solvents in coal liquefactions has been discussed by Oele et al[1]. Anthracene oil, for example, is a good solvent when used at a high temperature about 700°K; and the solvent itself can be recovered from the solution substantially unchanged. The action of solvent is presumed to facilitate thermal degradation of coal causing breakage of the coal into smaller and more readily dissolvable fragments. In recent years, many investigators[2, 3, 4, 5] have postulated that in the liquefaction process the hydrogen added to the coal is largely derived from the vehicle solvent such as recycle oil, anthracene oil or partly hydrogenated phenanthene. The function of hydrogen and catalyst is to subsequently re-hydrogenate the vehicle solvent. Once a part of the coal has been brought into the solution by physical dissolution or by partial hydrogenation, the molecular species derived from the coal can migrate in the solution where it can be further hydrogenated.

Curran et al[2] studied the kinetics of the transfer of hydrogen from tetralin to bituminous coal and coal extracts. They proposed that the dissolution is a first order reaction, and assumes that thermal decomposition of coal into free radical components occurs with the slowest characteristic rate constant. Klopper et al[4] noted a marked increase on coal dissolution as the partial pressure of hydrogen was increased in a batch autoclave system.

In this study a rate equation for dissolution of coal under hydrogen pressure is proposed which can describe fairly closely the experimental data reported by Pittsburg & Midway Coal Mining Company[6] and the University of Utah[7]. Data obtained by Colorado School of Mines[8] are used to compare the sulfur content in desulfurized coal.

University of Utah Coal Hydrogenation

The data on coal hydrosolvation, without catalyst, from the University of Utah are examined in this study.

Coal was slurried in a coal derived oil and was hydrotreated under hydrogen pressure in a batch stirred tank reactor. Experiments were performed in a temperature range of 400-500°C, under a hydrogen pressure of 0-2000 psig, with a residence time ranging from 2 to 30 minutes.

Analysis of the coal used is shown in Table 1. Examining the data reported, an empirical rate equation is proposed here which seems to represent the dissolution rates closely. The proposed rate expression has the form:

$$\begin{bmatrix}\text{rate of}\\ \text{dissolution}\end{bmatrix} = \begin{bmatrix}\text{rate}\\ \text{constant}\end{bmatrix} \cdot \begin{bmatrix}\text{fraction of undissolved}\\ \text{solid organics}\end{bmatrix} \cdot \begin{bmatrix}\text{coal-solvent}\\ \text{ratio}\end{bmatrix}$$

or $$r_A = k(C_{SO})\,(1-X)\left(\frac{C}{S}\right) \qquad X < 0.95 \qquad (1)$$

where r_A is the rate of dissolution in gm. per. hr. c.c. reactor volume,
C_{SO} is the weight fraction of organics in the untreated coal,
k is the dissolution rate constant in gm. per. hr. per c.c. reactor volume
X is the conversion, defined as (amount of solid organics dissolved)/(amount of solid organics in the untreated coal),
and $\frac{C}{S}$ is the coal to solvent (weight) ratio.

Integrating Equation (1) gives:

$$\ln(1-X) = -k\cdot\theta \qquad (2)$$

where θ for the batch reactor is defined as $(C_{SO})\left(\frac{t}{C_{ao}}\right)\left(\frac{C}{S}\right)$,
t is the reactor time in hours,
and C_{ao} is grams of ash free coal per c.c. of reactor volume. The value of C_{ao} is estimated to be 0.245 gm/c.c. for the Utah experiments.

The University of Utah's data are shown in Figure 1 in terms of $\ln(1-X)$ and θ as suggested by the above equation. Three hydrogen pressure levels were investigated and the effect of pressure on the dissolution rate constant, k, is shown in Figure 2. This figure suggests an exponential dependency of the rate constant of the hydrogen partial pressure. Incorporating the hydrogen pressure effect on the rate constant, and assuming an Arrhenius temperature dependency, the rate equation given by Equation (1) takes the form

$$r_A = k_o\mathrm{EXP}(-E/RT)\ \exp(0.000684\ P_{H_2})(C_{SO})(1-X)\left(\frac{C}{S}\right) \qquad (3)$$

where the dissolution rate constant, k, in Equation (1) and (2) is assumed to have the form $k = k_o\exp(-E/RT)\exp(\beta P_{H_2})$ and P_{H_2} is the partial pressure of hydrogen in psia.

The University of Utah's experimental data are then shown in Figure 3 plotted in the form suggested by Equation (2) and taking into account the hydrogen pressure dependency of the dissolution rate constant. In Figure 4 the temperature dependency of the dissolution rate constant is assumed, and the activation energy is found from the Arrhenius plot (given in Figure 5) to be about 11 Kcal/mole. Calculated conversions using the above activation energy are compared with experimentally reported conversions in Figure 6. It can be seen from this figure that the agreement is good.

Solvent Refined Coal (SRC) Process

The experimental data for the SRC process are taken from Pittsburg and Midway's monthly reports[6]. Raw coal was pulverized to -150 mesh and mixed with solvent (Table 2 gives the analysis of the coal used). The coal-solvent slurry was pumped together with hydrogen, through a preheat coil (an 18 foot length of high pressure tubing having 13/64 inch I.D.) to a reactor zone or "dissolver coil" (length to diameter ratio = 10:1). The dissolver was operated in a temperature range of 375-450°C and a pressure range of 1500-2000 psig, (a majority of the experiments were run at 1500 psig). The starting solvents for the experiments were carbon black feedstock (FS120) and anthracene type solvent.

Two modes of operation were studied: recycle and the single-Throughput mode. The recycle stream consisted of either unfiltered coal solution, or a mixture of unfiltered coal solution and distilled liquid product. The single throughput operation used the distilled liquid product from the previous experimental run as the solvent feed for the next run.

The performance equation for the plug flow reactor used in the SRC experiments is similar to the performance equations for a batch reactor used by the University of Utah given by Equation (2) if the quantity θ is redefined.

For the plug-flow reactor and single throughput operation Equation (2) becomes

$$\ln(1-X) = -k\cdot\theta' \qquad (4)$$

For the plug-flow reactor and the recycle mode operation integration of Equation (1) gives

$$\ln\left(\frac{1-X_2}{1-X_1}\right) = -k\cdot\theta' \qquad (5)$$

where $\theta' = \left(\frac{V}{F}\right)\left(\frac{C}{S}\right)(C_{SO})$ is in hr.-c.c./gm., V is the volume of the reactor in c.c., F is the mass flow rate of solid organics into reactor in gm. per hr., and X_1, X_2 are conversions at the entry and exit of a recycle reactor.

Based on Pittsburgh and Midway's data $\ln(1-X)$ or $\ln((1-X_2)/(1-X_1))$ was plotted as a function of θ', as shown in Figure 7. The slope of the line through the data represents the value of (-k). Assuming on Arrhenius dependency of the dissolution rate constant, k, on temperature (i.e., $k \alpha \exp(-E/RT)$, the slope of the curve of ln k versus 1/T (see in Figure 9) is equal to (-E/R). The value of the activation energy, E, is found to be 4.5 Kcal/mole with k_o = 15.34 gm/hr.-c.c. In calculating k_o the same dependence of the dissolution rate on the partial pressure of hydrogen that was observed for University of Utah's experiments was assumed for the Pittsburgh and Midway's experiments. This is a tentative assumption which must be varified by further experiments.

The small activation energy suggests that the rate of dissolution is probably controlled by the counter-diffusion of dissolved organic components from coal to solvent and the dissolved hydrogen in the solvent to the coal particle. Using the above value of the activation energy and the proposed rate expression conversions are calculated and compared with the experimental values reported by Pittsburgh and Midway as shown in Figure 9. Fairly good agreement between the two can be seen.

Colorado School of Mine Sulfur Removal Experiments

Colorado School of Mines performed a factorial experimental design on desulfurization of coal. Although, their experiments were not intented for kinetic studies of coal dissolution, the relation between the percent sulfur in desulfurized coal and total sulfur content of feed can be compared with that of Pittsburgh & Midway Co. as shown in Figure 11. It can be noted that the anthracene oil curve obtained from their experiments agrees closely with that of runs obtained by Pittsburgh & Midway Co. also from anthracene type solvent.

Discussion

The activation energy for diffusion of a non-polar chemical species in coal derived liquid can be estimated to be 4.3 to 6.0 kcal/gmole which is approximately in the range of the activation energy observed in the University of Utah's and Pittsburgh and Midway's coal dissolution experiments. Thus, it seems reasonable that the dissolution of coal in solvent-hydrogen mixtures may be diffusion controlled.

The rate of coal dissolution appears to be independent of the coal particle size distribution within the range of operating conditions considered. There is evidence[3] that liquefaction process is not a steady erosion of a coal particle, from the outside, but rathe the solvent penetrates the particle pores causing swelling and disintegration of the particles, exposing new surface at which dissolution can take place. Apparently for some coals, temperature above 370-390°C, the coal particles appear to puff up like popcorn and disintegrate into smaller fragements.

The linear dependence of the dissolution rate on the coal-solvent ratio, (C/S), is shown in Figure 10, in which the quantity $-\ln(1-X)/[k(V/F)(C_{S0})]$ is shown as a function of (C/S). This linear relation is observed for coal-solvent ratios ranging from 0.2 to 0.6.

Comparison of Figures 1 and 7 reveals that the rate constant from University of Utah's experimental runs is larger than that from Pittsburg and Midway's runs (see also Figure 21). A possible explanation for this difference is that the batch reactor with a stirring device probably had more tubulent contacting between solvent and coal particles (hence, high mass transfer coefficients) than the tubular reactor of Pittsburgh and Midway experiments. Furthermore, since the University of Utah and Pittsburgh and Midway used different coals factors such as rank of coal, geological history, and mineral content in ash could have affected liquefaction rate. In particular, mineral matter contained in the coal has been thought to catalyze coal dissolution.

In Solvent Refined Coal process and in most continuous coal liquefaction processes, a preheating section is usually required to heat the incoming feed stream of the dissolution reactor. It is possible that partial dissolution of the coal takes place in this section. Therefore, the contribution of the preheaten section in dissolving the coal should be considered in analyzing the dissolution kinetic.

Conclusions

(1) The coal dissolution data obtained from the Pittsburg and Midway Company and the University of Utah have been evaluated based on a proposed dissolution rate equation. The calculated conversions based on the proposed kinetic rate expression agree fairly closely with the experimental conversions reported by the University of Utah's coal hydrogenation experiments and Pittsburg and Midway's SRC experiment. The rate of dissolution for $x < 0.95$ can be represented by the following empirical equation.

$$r_A = k_o \exp(-E/RT)(C_{SO})(1-X)\left(\frac{C}{S}\right)\exp(0.000684 \cdot P_{H_2})$$

		Illinois, River King Coal	Kentucky No. 9 Coal
where	k_o	2125 gm/hr.-c.c.	15.3 gm/hr.-c.c.
	E	11 Kcal/g-mole	4.5 Kcal/g-mole

(2) The temperature effect on the rate constant for both processes has been examined and the activation energies for coal dissolution vary depending on the type of coal and contacting devices used. Based on the small activation energies calculated from experimental data, it is postulated that the rate of dissolution is probably controlled by the diffusion of some organic component from the coal surface into solvent-hydrogen mixture.

(3) The dissolution rate of coal appears to depended exponentially on the hydrogen partial pressure. However, further investigations are needed to validate this conclusion.

(4) A rough relation exists between the precent of sulfur in solid coal fed and the percent of sulfur remaining in desulfurized coal for a given type of solvent.

Acknowledgment

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TABLE 1

Analysis of Coal Used in the University of Utah's Coal Hydrogenation Experiments[7] Illinois, River King Coal.

Proximate	wt.%	Ultimate (maf)	wt.%
Moisture	5.6	Carbon	79.7
Ash	9.9	Hydrogen	5.4
Volatile Matter	36.7	Nitrogen	2.1
Fixed Carbon	47.8	Sulfur	3.8
	100.0	Oxygen (diff.)	9.0
			100.0

TABLE 2

Analysis of Coal Used in the SRC Process[6] Kentucky No. 9 Coal

Proximate	wt.%		Ultimate	wt.% (dry)	
Moisture	3.90	9.34	Carbon	70.56	72.76
Ash	11.33	8.40	Hydrogen	4.87	5.24
Volatile Matter	36.35	35.28	Nitrogen	1.48	1.63
Fixed Carbon	48.42	46.98	Chlorine	.07	.10
	100.00	100.00	Sulfur	4.27	3.35
			Ash	11.79	9.27
			Oxygen (diff)	6.96	7.65
				100.00	100.00

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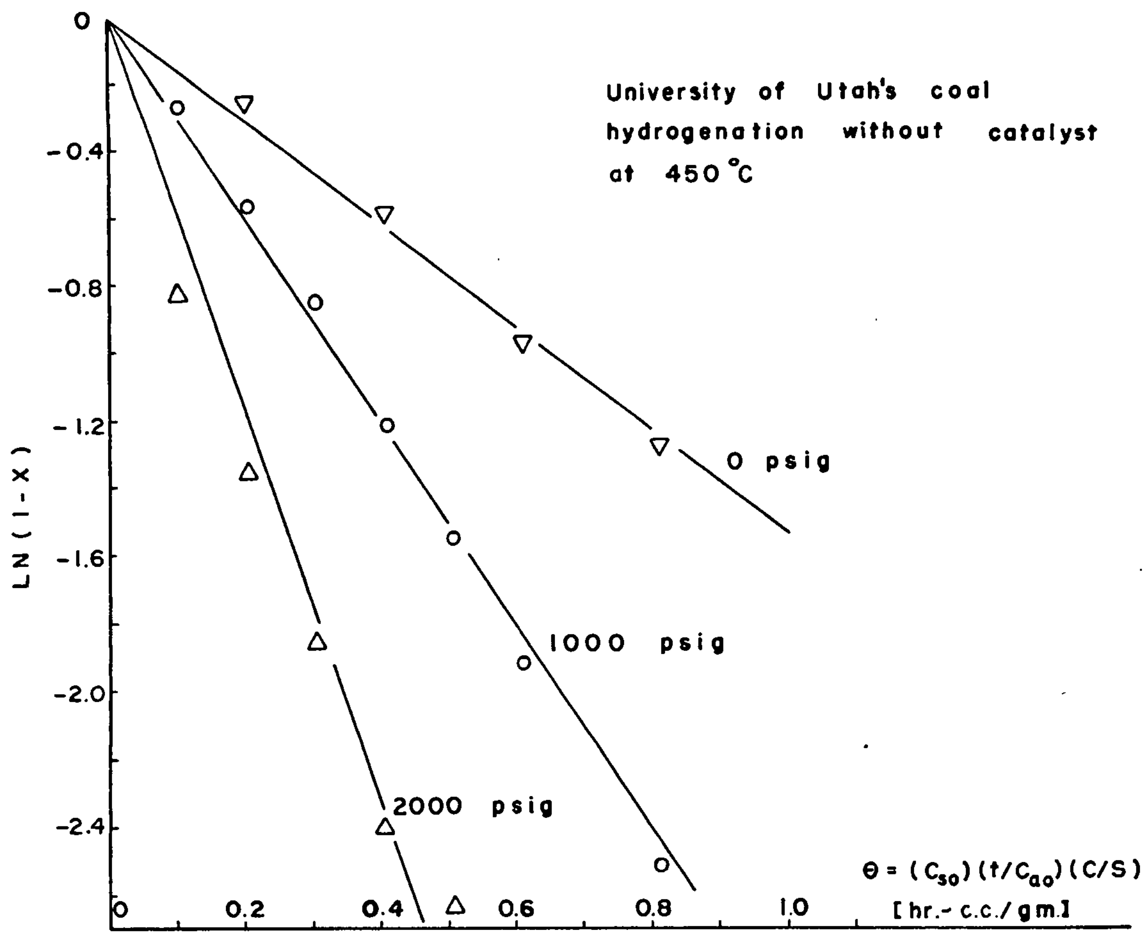

Figure 1 EFFECT OF HYDROGEN PARTIAL PRESSURE ON RATE CONSTANT.

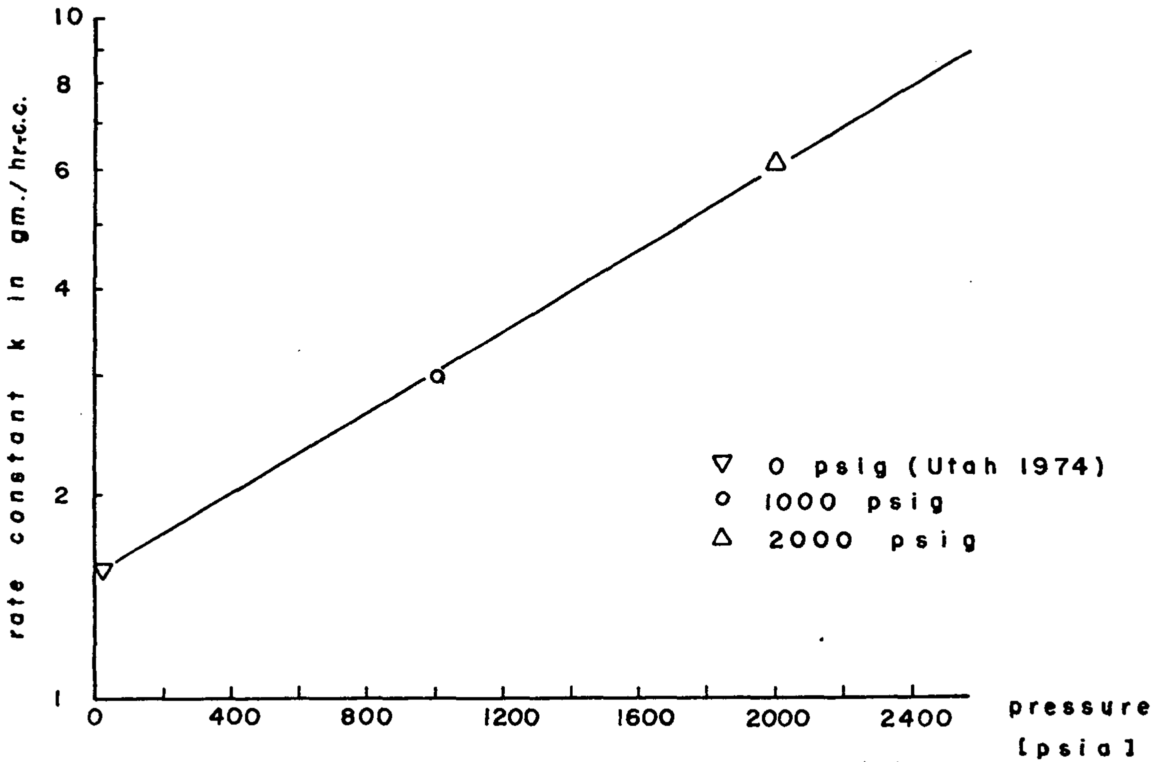

Figure 2 PRESSURE EFFECT ON RATE CONSTANT (Temp. = 450°C)

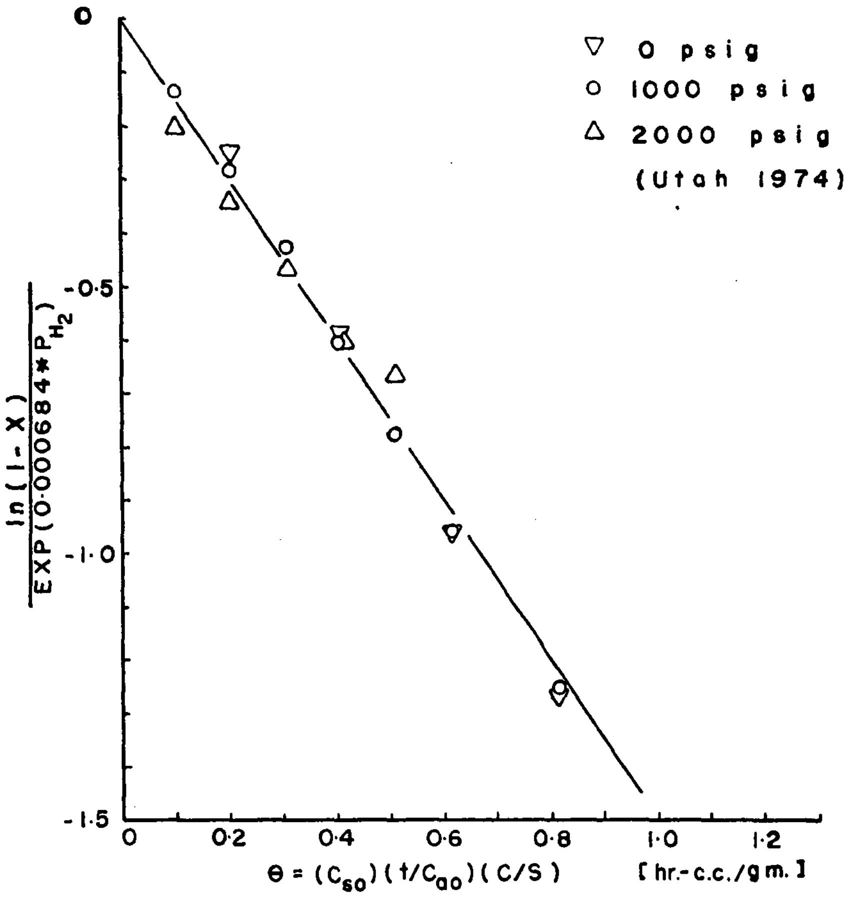

Figure 3 CORRELATION OF KINETIC RATE EQUATION ON COAL DISSOLUTION (Temp. = 450°C)

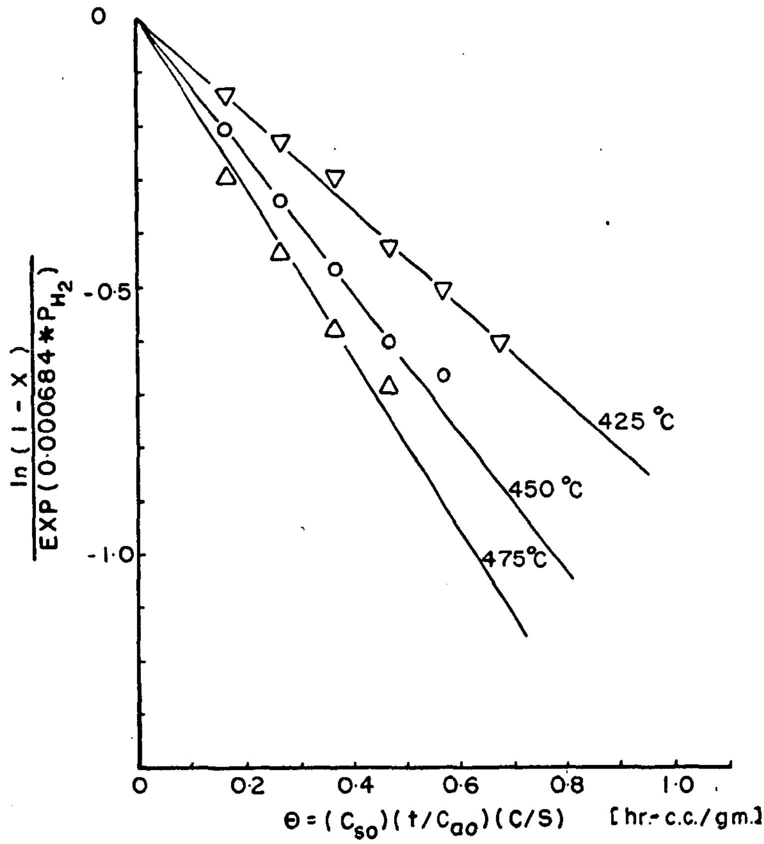

Figure 4 TEMPERATURE EFFECT ON RATE CONSTANT OF COAL DISSOLUTION (without catalyst)

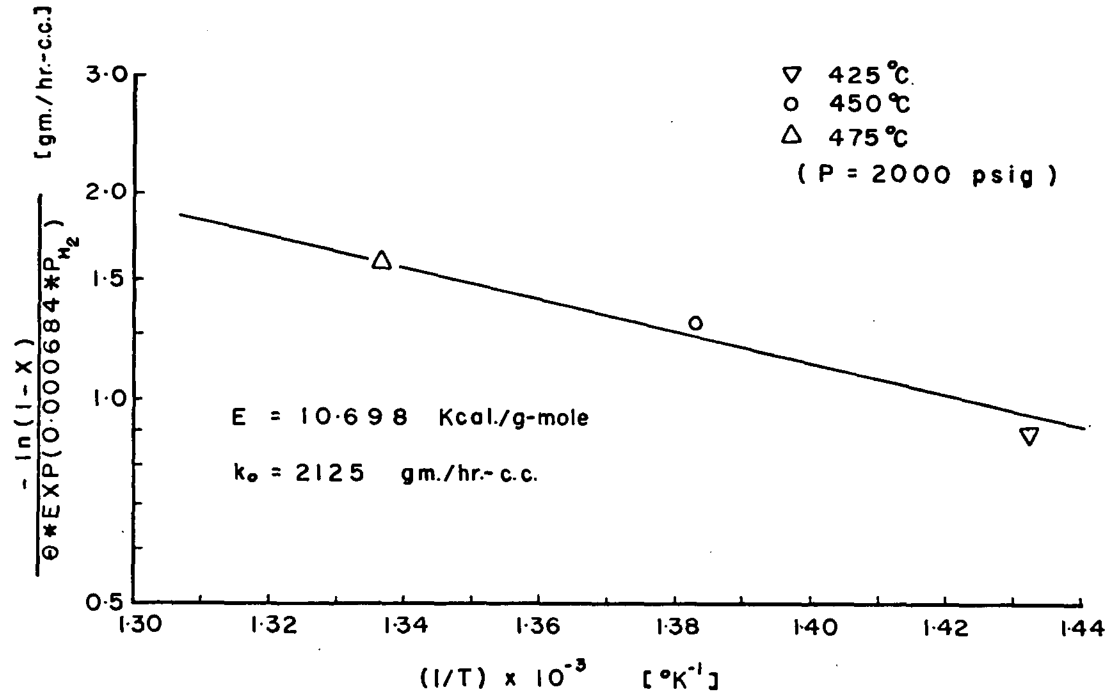

Figure 5 ARRHENIUS' PLOT FOR UNIVERSITY OF UTAH'S COAL HYDROGENATION EXPERIMENT (without catalyst)

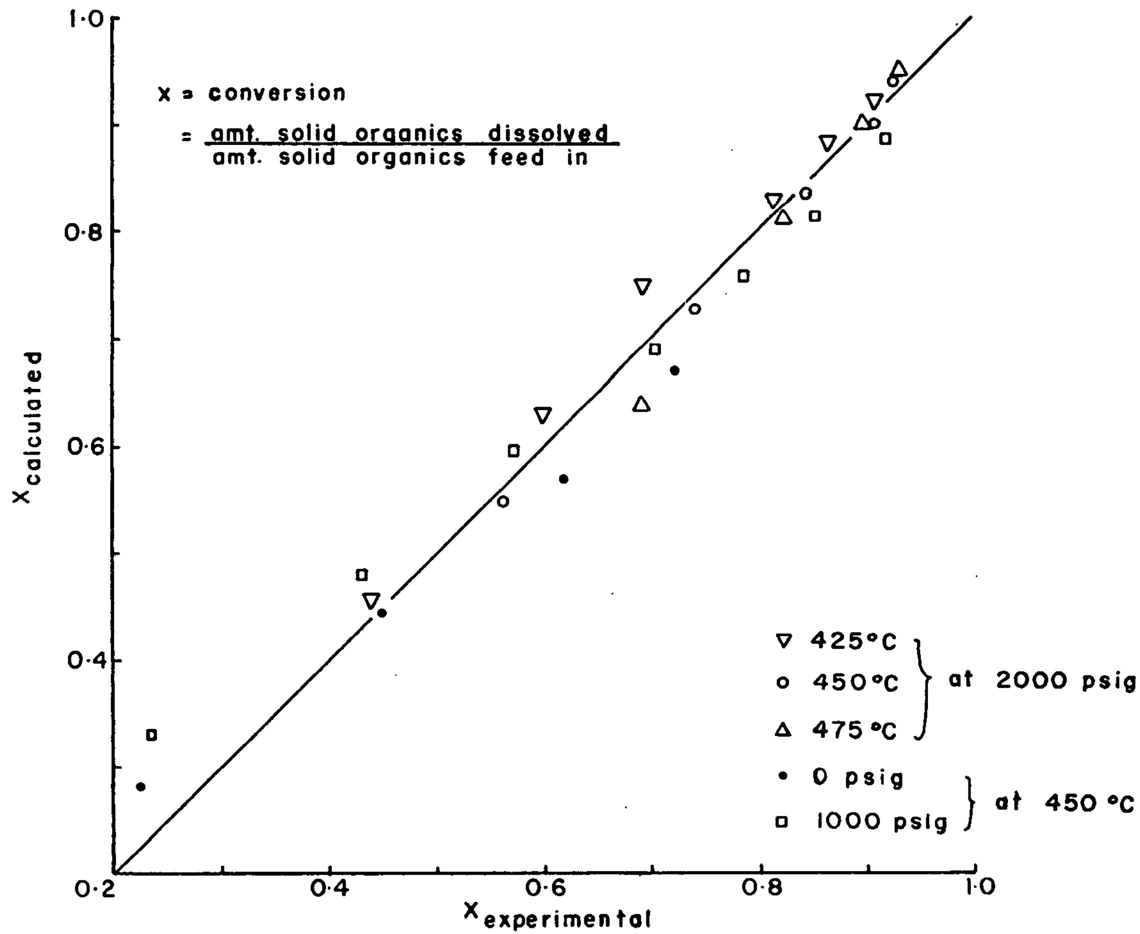

Figure 6 COMPARISON OF CALCULATED AND EXPERIMENTAL CONVERSION FROM UNIVERSITY OF UTAH'S COAL HYDROGENATION (without catalyst)

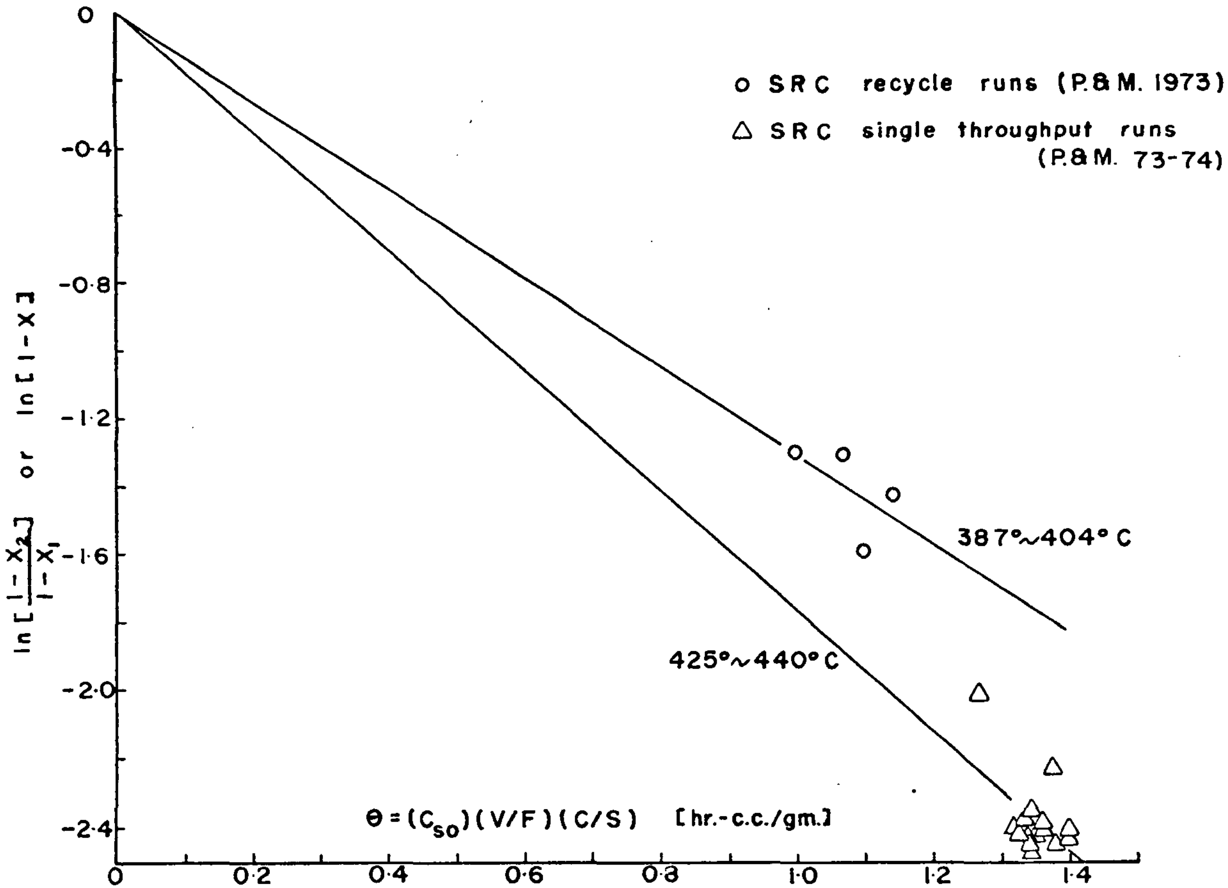

Figure 7 PLOT OF ln(1-X) vs. θ TO EVALUATE RATE CONSTANT.

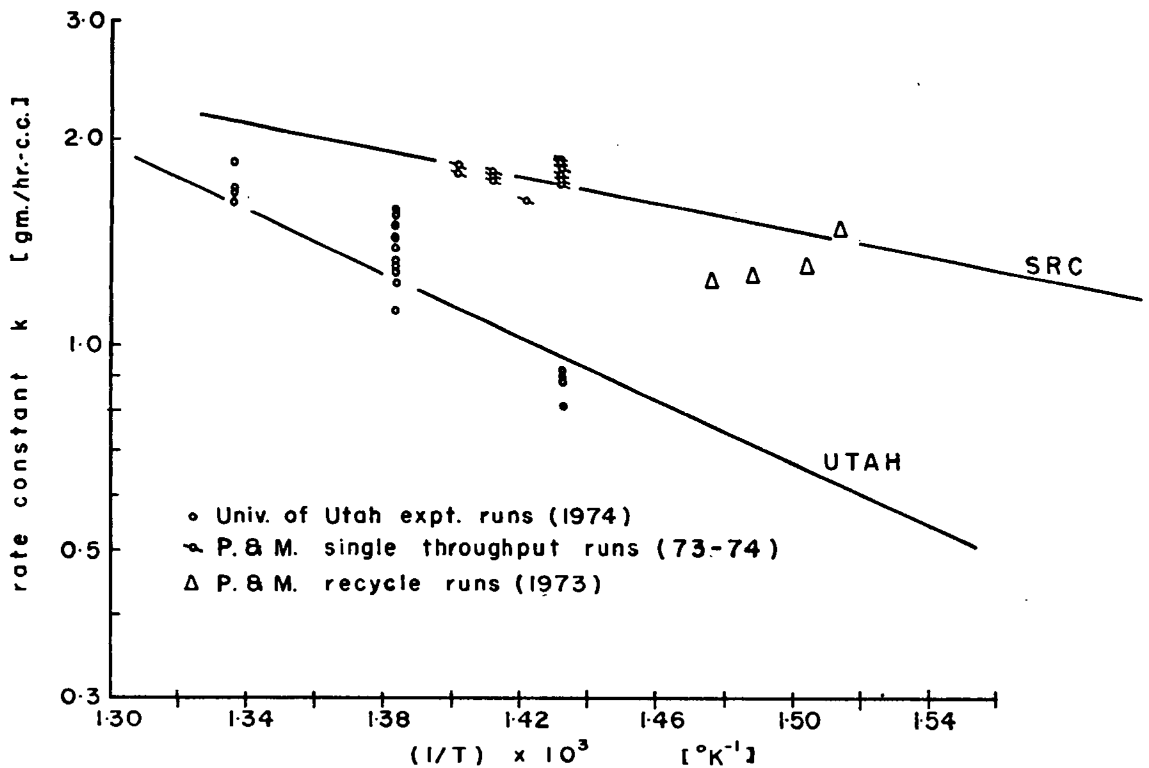

Figure 8 COMPARISON OF ARRHENIUS' PLOT FOR PITTSBURG & MIDWAY COMPANY DATA AND UNIVERSITY OF UTAH EXPERIMENTAL RUNS.

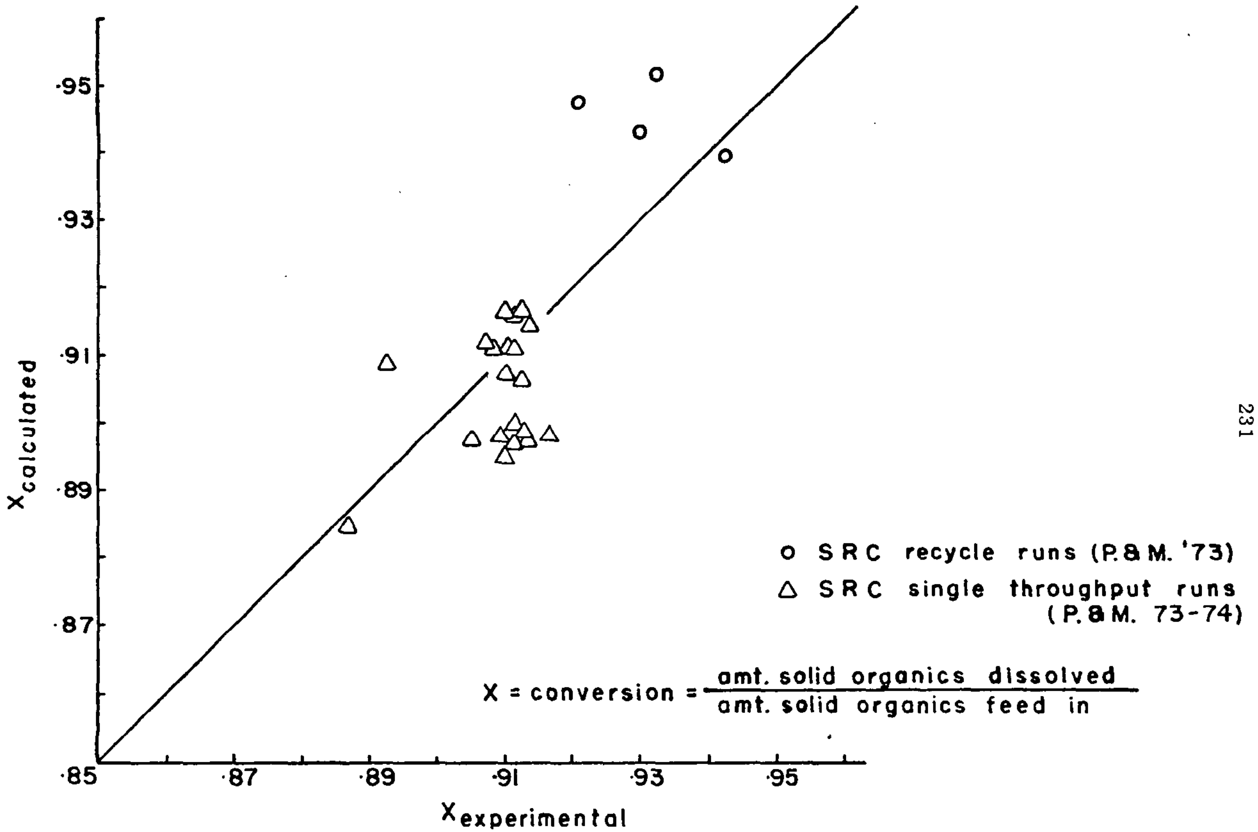

Figure 9 COMPARISON OF CALCULATED AND EXPERIMENTAL CONVERSION ON SRC PROCESS.

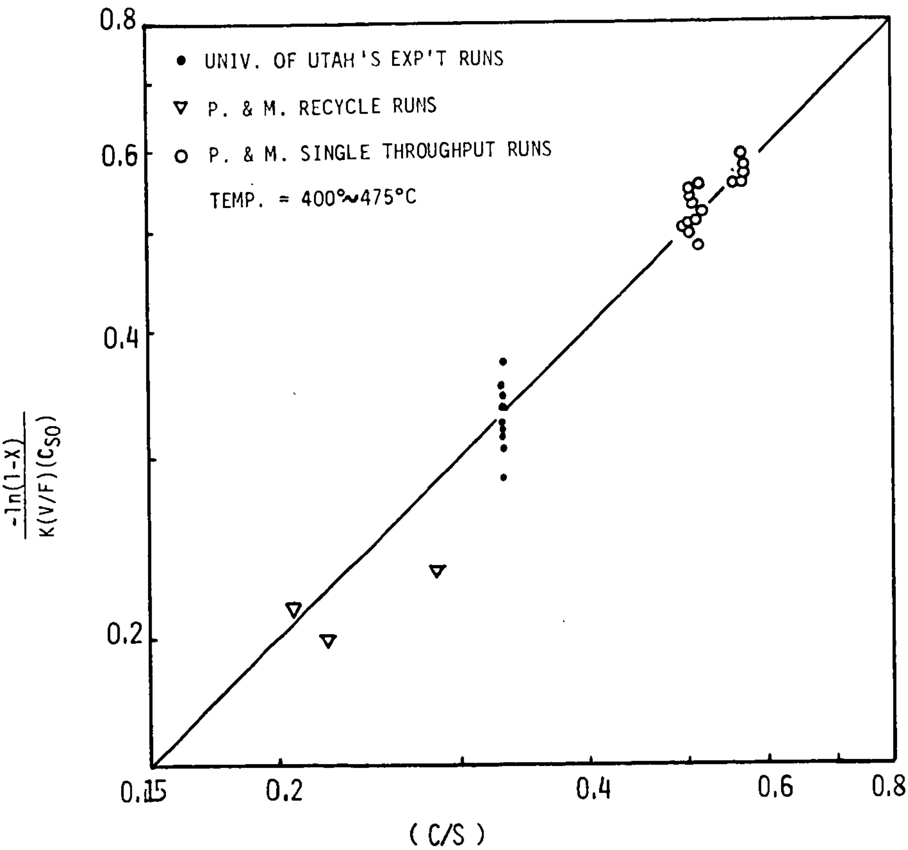

Figure 10 EFFECT OF COAL TO SOLVENT RATIO ON COAL LIQUEFACTION.

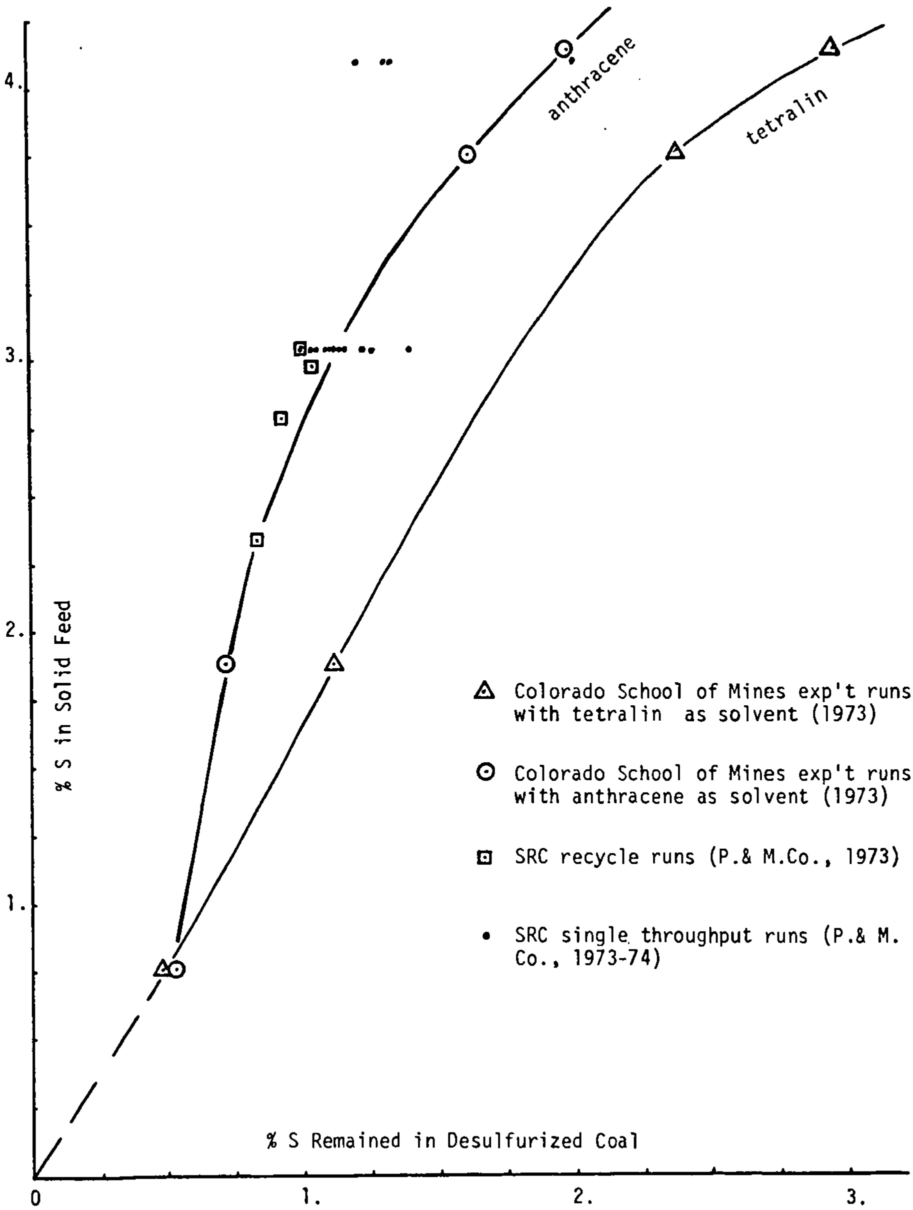

Figure 11. ESTIMATION OF SULFUR LEVELS IN DESULFURIZED COAL.

LOW SULFUR COAL OBTAINED BY CHEMICAL DESULFURIZATION FOLLOWED BY LIQUEFACTION

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The sulfur content of coal, nearly all of which is emitted as sulfur oxide during combustion is, on the average, about equally distributed between two chemical forms, inorganic (iron pyrites) and organic sulfur.

An unconventional approach for near total removal of the pyritic sulfur content of coal was recently reported by Meyers et al in this journal[1]. This new technique involves treatment of coal with a regenerable aqueous ferric solution as outlined in eqs 1 and 2[2]

$$FeS_2 + 4.6\ Fe_2(SO_4)_3 + 4.8\ H_2O \rightarrow 10.2\ FeSO_4 + 4.8\ H_2SO_4 + .8S \quad (1)$$

$$2.4\ O_2 + 9.6\ FeSO_4 + 4.8\ H_2SO_4 \rightarrow 4.8\ Fe_2(SO_4)_3 + 4.8\ H_2O \quad (2)$$

followed by a separation of generated elemental sulfur and iron sulfate. Subsequent laboratory investigations demonstrated that the process could reduce the sulfur content of 30-40% of the U.S. Appalachian coal reserves to the 0.7 to 0.8% sulfur level needed to meet the Ambient Air Quality Act [3].

Coal liquefaction (Figure 1A), the catalytic or non-catalytic hydrogenation of coal in a coal derived solvent to produce a utility fuel,[4] has been demonstrated to remove in the range of 40-60% or more of the organic sulfur from coal by conversion to hydrogen sulfide, and to be capable of removing nearly all of the inorganic sulfur and most of the ash if a suitable means for filtration of the micron-sized inorganic residue from the viscous liquefied coal could be developed. To date, the filtration technology necessary to accomplish the de-ashing of the liquefied coal and limited organic sulfur reduction have been the major problems associated with liquefaction, particularly with the non-catalytic version, known as solvent refined coal.

We have investigated the combination of the Meyers Process with a simplified form of coal liquefaction (Figure 1B) in order to begin to devise a potentially economical, viable combined process. In our approach, the filtration step is eliminated so that desulfurization is effected by a combination of first, ferric ion leaching to remove pyritic sulfur and second, hydrogenation to remove a significant portion of the organic sulfur as hydrogen sulfide. The product coal, however, contains the normal coal ash content less the pyrite which has been removed. This ash, which is also a pollutant when coal is combusted in a power plant, can be removed by available electrostatic precipitation and bag house techniques after combustion but prior to emission into the atmosphere(5).

We selected two coals, from the Muskingum (Meiggs Creek No. 9 seam) and the Camp (Ky No. 9 seam) mines, for our investigations as representative of the two major coal basins east of the Mississippi River, the Appalachian and Eastern Interior. The two mines are among the largest in the U.S. Samples of run-of-mine coal(6) were cleaned to remove rock fractions in order to represent the product normally obtained from mines after coal preparation(7).

The cleaned coals were then chemically desulfurized utilizing the Meyers Process and resulted in 93-98% removal of pyritic sulfur. Two samples of each chemically desulfurized coal and two samples of each untreated coal were subjected to identical and typical batch type coal liquefaction conditions[8] one hour residence time in 4 to 1 weight ratio of solvent to coal. The filtration step was omitted (Figure 1B) and the solvent was recovered. The results are tabulated in Table 1. Expts. 2 and 4, in which coal containing pyrite was charged to the reactor and Expts. 1 and 3, which had been chemically desulfurized prior to hydrogenation, show very similar organic sulfur reduction and heat content increase. In all cases the small amount of sulfate surfur present in the coal was destroyed during the hydrogenation process.

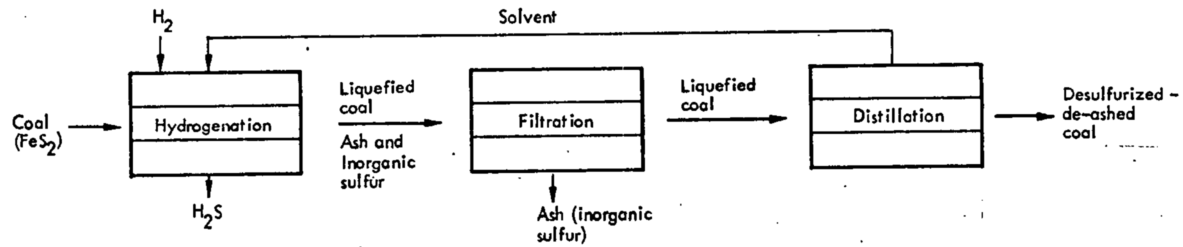
We conclude that (i) the presence or absence of pyrite does not materially affect either the hydrogenation of organic sulfur or the uptake of hydrogen by the coal matrix as reflected in the organic sulfur and btu changes, respectively; (ii) nearly all of the pyrite, when present in the coal samples (Expts. 2 and 4), is converted under the hydrogenation conditions to iron sulfide and hydrogen sulfide as in eq 3,

$$FeS_2 + H_2 \rightarrow FeS + H_2S \qquad (3)$$

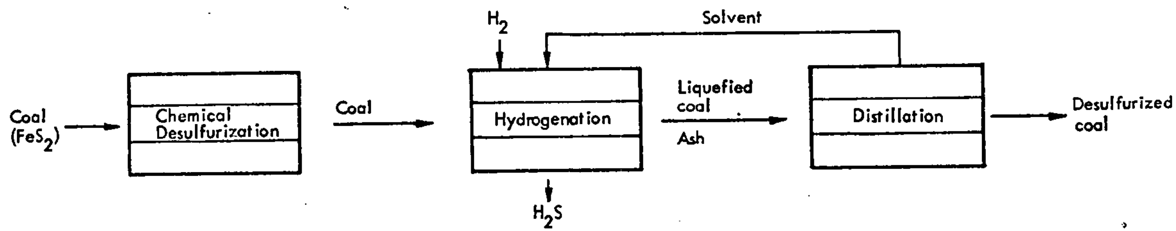
as has been shown for mineral pyrite under similar conditions[9]; and (iii) the two coal samples, although from different coal basins, behaved similarly under hydrogenation conditions.

It is notable to point out that the Ky. No. 9 (Camp) coal was reduced to 0.85% total sulfur (Expt. 3) with a heat content increase to 14156 btu, by the combination of chemical desulfurization and hydrogenation, meeting the requirement of 0.6 lb sulfur/10^6 btu established by the Federal Ambient Air Quality Act for power plant fuel for new stationary sources. Thus, this coal could meet the federal standard utilizing the combined process.

It therefore appears that a combination of the Meyers Process with a simplified form of coal liquefaction, as described in Figure 1B, is technically feasible for the desulfurization of coal to meet pollution control standards[10,11].



A. Coal Hydrogenation and De-ashing



B. Chemical Desulfurization Followed by Coal Hydrogenation

Figure 1. Process flow charts: A. (i) coal containing pyrite is slurried with a coal derived solvent with or without a catalyst, hydrogenated at about 400°C/1000-4000 psig; (ii) undissolved coal, ash and any catalyst is filtered away from the dissolved coal and solvent; (iii) solvent is recovered by distillation to give a desulfurized, de-ashed coal; B. filtration step is omitted to give a desulfurized coal which has most of its iron removed but is not de-ashed.

Table 1. Data on sulfur reduction. Each coal (cleaned) was pulverized to -100 mesh for sampling and processing. Chemical desulfurization was performed at 102° by treatment with aqueous 1N ferric sulfate solution as described in reference 3. Hydrogenation was performed at 425°/2000 psig in anthracene oil solvent as described in reference 7. Solvent was recovered ± 3% by multiple repulverization and solvent distillation at 300°C maximum, 3 mm Hg ultimate.

Expts. no.	Coal*	Treatment	Dry forms of sulfur (% by weight) of Total*	Pyritic	Sulfate	Sulfide†	Organic‡	Organic sulfur reduction (% by weight)	Heat content btu	Increase in heat content (%by weight)
	Musk		4.37	1.70	0.11	0.00	2.56		11829	
	Musk	chem desulfurized	3.14	0.12	0.08	0.00	2.94		12077	
1	Musk	chem desulfurized and hydrogenated	1.24	0.01	0.00	0.00	1.20	59 ± 2	13180	9 ± 2
2	Musk	hydrogenated only	1.95	0.06	0.00	0.76	1.13	56 ± 2	12904	9 ± 1
	Camp		2.98	0.81	0.30	0.00	1.87		12752	
	Camp	chem desulfurized	2.26	0.02	0.28	0.00	1.96		12956	
3	Camp	chem desulfurized and hydrogenated	0.85	0.01	0.00	0.00	0.84	57 ± 0	14156	9 ± 2
4	Camp	hydrogenated only	1.35	0.08	0.00	0.32	0.95	49 ± 3	13545	6 ± 2

*Total, pyritic, sulfate sulfur and heat content (dry basis) were determined by American Society for Testing Materials techniques at the Commercial Testing and Engineering Laboratories, Chicago, Illinois. The values reported for treated coals are averages for duplicate runs. †Sulfide sulfur was determined by total sulfur analysis of coal after 1 hr extraction with boiling 5N hydrochloric acid, the difference in sulfur content between extracted and unextracted coal, less the sulfate content determined by sulfate analysis of the acid solution being the sulfide sulfur. ‡Organic sulfur is the difference between total sulfur and the sum of pyritic, sulfate and sulfide sulfur.

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5. The ash remaining in liquefied coal derived from conventional liquefaction, although usually under 0.5% by weight of coal, is in the form of fine particles which may be environmentally hazardous and might also need to be precipitated prior to emission from a power plant.

6. Detailed analyses of the run-of-mine samples are presented in reference 3.

7. Run-of-mine coal samples crushed to -14 mesh were suspended in a 1.75 specific gravity liquid. The float material, 80-90% by weight was recovered as the "clean" fraction.

8. J.H. Gary, R.M. Baldwin, C.Y. Bao, M. Kirchner and J.O. Golden, "Removal of Sulfur from Coal by Treatment with Hydrogen". Prepared for Office of Coal Research, S/N 2414-00070, U.S. Government Printing Office, Washington D.C. (1973).

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10. It occurred to us that the filtration step in coal liquefaction could also be eliminated by extraction of iron sulfide with hydrochloric acid following liquefaction. However we have found that hydrochloric acid, in environmentally unsound amounts (about 1% W/W), remains with coal after treatment even after exhaustive washing with boiling water. A matrix of 1-hour sulfuric acid leaches to remove iron sulfide was attempted after it was found that 1N sulfuric acid dissolved pure iron sulfide in near quantitative yields. However we found no decrease in total sulfur for the Camp coal from Expt. 4 and only a slight decrease for the Muskingum coal from Expt. 2, after extraction with either 1N, 3N or 12N sulfuric acid. Thus, it does not appear feasible to chemically remove iron sulfide after liquefaction as a method for production of low sulfur fuel.

11. The finding that residual sulfate is destroyed during hydrogenation, together with the known high reactivity of elemental sulfur with hydrogen, indicates that the elemental sulfur and iron sulfate removal

steps of the Meyers Process could possibly be deferred to the hydrogenation step as a further combined process simplification.

12. Liquefaction studies were supported by Office of Coal Research Contract 14-32-001-1225. Conceptual development and all other experimental work were supported by TRW Inc.